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# Hydrogen Uptake of DPB Getter Pellets

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## **ABSTRACT:**

The physical and chemical properties of 1,4-diphenylbutadiyne (DPB) blended with carbon-supported Pd (DPB-Pd/C) in the form of pellets during hydrogenation were investigated. A thermogravimetric analyzer (TGA) was employed to measure the kinetics of the hydrogen uptake by the DPB getter pellets. The kinetics obtained were then used to develop a semi-empirical model, based on gas diffusion into solids, to predict the performance of the getter pellets under various conditions. The accuracy of the prediction model was established by comparing the prediction models with independent experimental data on hydrogen pressure buildup in sealed systems containing DPB getter pellets and subjected to known rates of hydrogen input. The volatility of the hydrogenated DPB products and its effects on the hydrogen uptake kinetics were also analyzed.

## INTRODUCTION:

Organic getters such as 1,4-diphenylbutadiyne (DPB) have a rapid and irreversible hydrogen uptake capability as well as a substantial hydrogen uptake capacity. The knowledge of the hydrogen uptake kinetics of such materials allows the prevention of hydrogen gas accumulation in sealed containers, which may lead to hydrogen corrosion of nuclear materials, undesirable effects on electronic components, or explosion hazard.<sup>1,2,3</sup> However, there are only a few published studies on the kinetics of the gettering or scavenging of hydrogen by DPB getter.<sup>4-6</sup> In this report, the physical and chemical properties of DPB blended with carbon-supported Pd (DPB-Pd/C) in the form of pellets were examined. The hydrogen uptake kinetics of these getter pellets were obtained with a thermogravimetric analyzer (TGA) under isobaric, isothermal conditions. The kinetics obtained were then used to develop a semi-empirical model, based on gas diffusion into solids, to predict the hydrogen uptake performance of the getter pellets at lower hydrogen pressure conditions. The accuracy of this kinetic prediction model was established by comparing the predictive results with independent experimental data on hydrogen pressure buildup in sealed systems containing DPB getter pellets with known rates of hydrogen input. The volatility of the hydrogenated DPB products and its effects on the hydrogen uptake kinetics were also included in the prediction model. The unique approach to the hydrogen uptake kinetic measurement and prediction for DPB-Pd/C pellets as presented in this report serves to complement the meager current database on the efficiency of the DPB getter pellets during service life.

## EXPERIMENTS:

In this report, the term “virgin DPB” implies unreacted DPB while the term “fully hydrogenated DPB” refers to 100 % reacted DPB (also called 1,4-diphenylbutane). Some experiments were performed on commercial virgin DPB crystallites purchased from Aldrich Chemical Company, Inc., some others on fully hydrogenated DPB crystallites bought from Alfa Aesar, but most of the work was done with DPB pellets manufactured by the Kansas City Plant, HoneyWell FMT. These DPB pellets have a composition of 75 wt% DPB and 25 wt% catalyst (5 wt% Pd on activated carbon). The role of the nanometer scale Pd catalyst is to split molecular hydrogen into atomic hydrogen for DPB molecules, which do not interact with molecular hydrogen, to uptake. The activated carbon support has a very high specific surface area ( $1100 \text{ m}^2/\text{g}$ ) and serves to spread the Pd catalyst throughout the DPB pellet structure. The DPB pellets are right circular cylinders with a diameter of approximately 2.8 mm, height of 3.1 mm and an axial hole through the pellet with a diameter of about 0.89 mm. Both virgin and fully hydrogenated DPB crystallites are white. The dark color of the DPB pellet is simply the result of the presence of carbon.

To assess the volatility of DPB getter pellets during service, the equilibrium vapor pressures of commercial virgin DPB crystallites, virgin DPB pellets and fully hydrogenated commercial DPB crystallites were measured by the technique of effusion thermogravimetry using a Cahn Versatherm vacuum microbalance with a base pressure in the range of 100mPa - 200 mPa. The Knudsen cells used in the effusion thermogravimetry were fashioned from gold foil with a thickness of 0.05 mm and had orifices ranging from 0.28 mm to 0.52 mm.

The kinetics of hydrogen uptake by DPB pellets were obtained under isothermal, isobaric conditions by recording the weight change with the Cahn Versatherm vacuum microbalance. Fig. 1 shows the chemical formulae for virgin DPB and fully hydrogenated DPB molecules. Each DPB molecule (molecular weight of 202 g/mol) can uptake a maximum of 8 hydrogen atoms. The reaction of DPB with atomic hydrogen is exothermic, but it was found experimentally (by embedding thermocouples into the different parts of the DPB pellets) that isothermal conditions (temperature fluctuation of less than 1 K) could be achieved if the experiments were carried out in one atmosphere of a premixed gas composed of 18 % or less hydrogen with the balance being helium. The pseudo-isobaric condition for the experiment was achieved by connecting the Cahn microbalance to a large premixed H<sub>2</sub>/He gas reservoir (approximately 0.2 m<sup>3</sup> total volume) such that the total amount of hydrogen consumption throughout the microbalance weight gain experiments (containing from 1-5 DPB pellets) was less than 0.1 % of the initial H<sub>2</sub> inventory in the reservoir. For practical purposes, the DPB pellet experiments described above could be considered to have been carried out in an isothermal, isobaric condition. To take into account the volatility of hydrogenated DPB during hydrogen uptake, another set of experiments was performed in which the hydrogenation progress was deliberately stopped (by removing the H<sub>2</sub>/He premixed gas and replacing it with pure He) at 5 wt%, 10 wt%, 20 wt%, etc. and the weight loss versus time (due to the volatility of the hydrogenated product) was measured.

A combination of the empirical kinetic data taken from the microbalance experiments and some common properties of all processes involving gas diffusion into solids formed the basis for kinetic predictions of hydrogen uptake under varying

conditions and will be presented in detail in the next section. The accuracy of the predictive model was established by comparing the predictions with independent experimental data on hydrogen pressure buildup in sealed systems containing DPB getter pellets and subjected to known rates of hydrogen input. The hydrogen pressure buildup in these sealed containers was measured with MKS Baratron gauges (absolute pressure transducers) and the hydrogen input was fixed at some constant rate with the use of a MKS mass flow controller, which could be varied from 0.001 standard cubic centimeters per minute (sccm) to 0.2 sccm.

The morphologies of the DPB pellets as a function of hydrogenation levels were also probed with a commercial digital camera and a scanning electron microscope (SEM) in secondary electron mode. For all optical and SEM images, the samples were removed from the hydrogenation chamber and transported in laboratory air to the digital camera or SEM work station. The handling, transportation and even storage of the DPB getter pellets in air do not affect its performance.

To obtain chemical structure information,  $^1\text{H}$  liquid state nuclear magnetic resonance (NMR) experiments were performed on a Bruker Advance 500 MHz spectrometer with a tunable broad band inverse (TBI) probe. All spectra were recorded at room temperature in  $\text{CD}_2\text{Br}_2$ .

## RESULTS & DISCUSSION:

The vapor pressure,  $P$ , is calculated from the rate of weight loss assuming effusive flow through the orifice of the Knudsen cell by the equation:

$$P = \frac{1}{[A \cdot f]} \frac{dw}{dt} \sqrt{\frac{2\pi kT}{m}} \quad (1)$$

In equation (1),  $k$  is Boltzmann's constant,  $T$  is temperature,  $A$  is the orifice area,  $m$  is the mass of the vaporizing molecule,  $dw/dt$  is the mass rate of effusion and  $f$  is the Clausing factor [ $f = 1 - 0.5(l/r) + 0.2(l/r)^2$  where  $l$  and  $r$  are the orifice length and radius, respectively]. Once a series of equilibrium vapor pressures at different temperatures was obtained, the Clausius-Clayperon equation was used to derive the enthalpy and entropy of vaporization ( $\Delta H_{vap}$  and  $\Delta S_{vap}$ ) according to equation (2).

$$\ln\left(\frac{P}{P_0}\right) = -\frac{\Delta H_{vap}}{RT} + \frac{\Delta S_{vap}}{R} \quad (2)$$

In equation (2),  $R$  is the molar gas constant and  $P_0$  is the vapor pressure at boiling point (one atmosphere). A linear fit through the plot of  $\ln(P/P_0)$  vs.  $1/T$  yields values of  $\Delta H_{vap}$  and  $\Delta S_{vap}$ . It can be observed from Fig. 2 that the vapor pressures of virgin DPB pellets were more scattered and somewhat lower than those of commercial virgin DPB crystallites. So, one effect of mixing the 25 wt% Pd/C catalyst with DPB was to effectively lower the vapor pressure of DPB in comparison with that of pure DPB crystallites. It is also seen from Fig. 2 that the vapor pressures of fully-hydrogenated DPB crystallites were significantly higher than those of their virgin counterparts. At 303 K, the equilibrium vapor pressure of fully hydrogenated DPB is close to 0.1 Pa, demonstrating that it is very volatile even at modest temperatures. Fig. 3 shows the plots of  $\ln(P/P_0)$  vs.  $1/T$  for virgin DPB crystallites, virgin DPB pellets, and fully hydrogenated DPB crystallites. From this plot, the values of  $\Delta H_{vap}$  and  $\Delta S_{vap}$  were obtained and are presented in table I. From the table and equation (2), it is clear that it is the combination of a low  $\Delta H_{vap}$  value and a high  $\Delta S_{vap}$  value that makes fully hydrogenated DPB more volatile than virgin DPB crystallites and virgin DPB pellets. Once  $\Delta H_{vap}$  and  $\Delta S_{vap}$  were obtained,



equation (2) can also be used to calculate the equilibrium vapor pressure at any temperature.

**Table I: Enthalpy and entropy of vaporization for the different types of DPB under study**

	Virgin DPB crystallites	Virgin DPB pellets (75 wt% DPB and 25 wt% Pd-C)	Hydrogenated DPB crystallites
$\Delta H_{vap}$ (J/mol)	111060	121985	113336
$\Delta S_{vap}$ (J/mol)	215	257	256

The connection between the equilibrium vapor pressure of a material and its volatility can be seen from the Langmuir-Knudsen evaporation rate equation:

$$J_v = \sigma \frac{(P_{equi} - P_a)}{\sqrt{2\pi mkT}} \quad (3)$$

In equation (3),  $J_v$  is the net vaporization flux in molecules per unit area per unit time,  $\sigma$  is the vaporization coefficient which depends on the material under study and its surface finish, while  $P_{equi}$  and  $P_a$  are the equilibrium and actual vapor pressures, respectively, over the evaporating surface. From equation (3), it is expected that a product with a high equilibrium vapor pressure suffers significant weight loss due to the vaporization of its molecules at the surface into the surrounding environment. Consequently, the study of the kinetics of hydrogen uptake of DPB through weight gain measurements must take into account the weight loss due to the high volatility of the hydrogenated product.

From this point on, the report is concerned only with the DPB pellets (75 wt% DPB + 25 wt% Pd/C catalyst). SEM images of virgin DPB pellets at different magnification levels are shown in Fig. 4. The inset of Fig. 4 shows an optical image of virgin DPB pellets. The pellets were solid with the dimensions described in the experimental section. The bottom two SEM images show the morphology at the outer surface of the virgin DPB pellets.

The top two SEM images reveal the porosity in the structure of the DPB pellets as observed from the cross-section of a DPB pellet which was broken in half. Note that the porosity observed in the broken virgin DPB pellet is closed (not an open porosity structure for gas molecules to move through like in the case of a sponge). The left column in Fig. 5 presents SEM images at the outer surface of a DPB pellet at ~ 25 wt% hydrogenation, while the right column in Fig. 5 contains the optical images of another DPB pellet at ~ 75 wt% hydrogenation. Clearly, at high hydrogenation levels, the pellet had softened considerably. The washout spot near the middle of the upper left SEM image in Fig. 5 was an artifact formed when the electron beam in the SEM was focused on that spot of the roughly 25 wt% hydrogenated DPB pellet. This pellet also looked partially liquefied, albeit not to the drastic level seen at 75 wt% hydrogenation. In fact, all DPB pellets that have been hydrogenated to beyond a few weight percent exhibited increasing level of liquefaction with further hydrogenation, even when observed by eye.  $^1\text{H}$  NMR investigations revealed the existence of four different hydrogen configurations in a ~ 52 % hydrogenated DPB pellet sample, including a fully hydrogenated state and three partially hydrogenated states. All of the  $^1\text{H}$  NMR configurations are shown in Fig. 6. In this figure, the peaks at ~ 7.5 ppm (or part per million) and ~7.6 ppm are  $^1\text{H}$  NMR associated with the aromatic protons on the phenyl ring of the DPB molecules. The peaks at 1.9 ppm and 2.9 ppm are  $^1\text{H}$  NMR associated with aliphatic protons ( $\text{CH}_2$ ) attached to the phenyl rings in the fully hydrogenated DPB structure. The doublets near 3.7 ppm and 6 ppm are associated with the protons in the CH groups belonging to partially hydrogenated DPB molecules containing 6 hydrogen atoms. The doublets near 6.7 ppm, and 6.9 ppm are associated with the protons in CH groups belonging to partially

hydrogenated DPB molecules containing 4 hydrogen atoms. Partially hydrogenated DPB molecules with only two hydrogen atoms produce only a  $^1\text{H}$  NMR doublet at  $\sim 6$  ppm. The peak at  $\sim 5.3$  ppm is from the  $^1\text{H}$  NMR of  $\text{CD}_2\text{Br}_2$  solvent. Thus, partially hydrogenated DPB pellets show the presence of partially and fully hydrogenated DPB molecules. Unfortunately, the effect of how chemical changes might induce the liquefaction of partially hydrogenated DPB pellets, while a subject of some interest, is beyond the scope of this work.

The top right image in Fig. 7 is a digital camera image of fully hydrogenated DPB pellets which were the result of leaving these pellets in a closed chamber with roughly 6000 Pa of hydrogen for a few weeks. The rest of Fig. 7 represents SEM images of fully hydrogenated DPB pellets at different magnification levels. Fully hydrogenated DPB pellets are solid just as the 100 % reacted DPB crystallites obtained commercially from Alfa Aesar. However, unlike the virgin DPB pellets, the fully hydrogenated DPB pellets were friable upon being touched. Most fully hydrogenated DPB pellets had elongated or squashed shapes. Many even fused together where they touched. Clearly, in going from the virgin state to fully hydrogenated state, the DPB pellets have gone through some dramatic changes which would be expected to result in a constantly changing vaporization coefficient  $\sigma$ . All these complexities make the quantification of the weight loss of hydrogenated DPB pellets as a function of hydrogenation level using the Langmuir-Knudsen formulation in equation (3) impractical. Instead, the weight loss was measured directly as a function of hydrogenation level. In a series of microbalance experiments, a  $\text{H}_2/\text{He}$  gas mixture was used to bring DPB pellets to certain predetermined hydrogenation level (e.g. 5 wt%, 10 wt%, 20 wt%, etc.). At this moment, the reaction was

halted by pumping out the H<sub>2</sub>/He gas and replacing it with pure He. The weight loss versus time due to the volatility of the hydrogenated product was then measured during the first few minutes after the microbalance had recovered from the perturbation of the gas change. In Fig. 8, a plot of the weight loss rate of hydrogenated DPB pellets as a function of the apparent hydrogenation percentage (before correction for product volatility) at ~ 294 K as recorded by the TGA is presented. From this plot, it is observed that the volatility of the hydrogenated DPB pellets increases with increasing level of hydrogenation up to around 20 % hydrogenation level, after which the degree of volatility decreases. This observation is in qualitative agreement with the morphology changes seen during the process of hydrogenation of the DPB pellets presented in Figs. 4-7 for the following reasons. As the hydrogenation process went on, the rate of weight loss increased due to the formation of the more volatile hydrogenated product. As the DPB pellets got hydrogenated further, they also became more liquefied. At around 20 % hydrogenation level, the liquefaction must have progressed enough to effectively reduce the surface area available for vaporization of the hydrogenated product resulting in a decrease in the rate of weight loss. At ~ 65 % hydrogenation level, the liquefaction apparently reached a saturation level, and the rate of weight loss was roughly constant thereafter. It is noted that the difference in the rates of weight loss due to the volatility of virgin DPB pellets and the highly hydrogenated DPB pellets (Fig. 8) is not quite the same as the difference in the equilibrium vapor pressures measured for virgin DPB crystallites and fully hydrogenated DPB crystallites (Fig. 2). This was probably due to changes in the porosity structure, grain sizes, and surface area available for vaporization of the DPB pellets in going through liquefaction during the hydrogenation process and re-

solidification near the completion of this process. The observed error bar associated with the data points in Fig. 8 was  $\sim 35\%$  and was due to a combination of pellet to pellet variation and experimental error.

In Fig. 9(a) and (b) are shown the plots of the hydrogenation percentage vs. time and the hydrogen uptake rate per pellet vs. corrected hydrogenation percentage curve for typical isobaric, isothermal hydrogen uptake experiments with DPB pellets at 294 K. The gas used in this experiment had a total pressure of one atmosphere and was composed of 10 % hydrogen with the balance being helium. In Fig. 9 (a), the dashed and solid curves represent the hydrogenation vs. time curves prior to and after the correction for weight loss due to the volatility of the hydrogenated products, respectively. The correction for weight loss due to the volatility of the hydrogenated products was achieved by adding the weight loss as a function of hydrogenation level to the apparent weight gain curves due to hydrogen uptake.

It should be noted that the weight loss due to the volatility of the hydrogenated product will cease when the equilibrium vapor pressure of the reacted product is reached. So, corrections for the volatile nature of the reacted product should be much smaller in closed systems with smaller volumes. The hydrogenation percentage vs. time curve presented in Fig. 9(a) displays fairly abrupt changes at around 40 % and 85 %. The hydrogen uptake rate per pellet vs. corrected hydrogenation percentage curve in Fig. 9(b) shows even more abrupt rate changes at around 10 %, 40 % and 85 %. The performance of the DPB getter reached its lowest level beyond 60 % consumed capacity, but increased again around 85 %. This increase in performance is attributed to the onset of the re-solidification of heavily hydrogenated DPB molecules on the high surface area of the

carbon support. This phenomenon causes an increase in the surface area available for  $H_2$  adsorption as well as for vaporization of hydrogenated products, resulting in a jump of the hydrogen gettering rate near the end of life of the DPB pellets. Obviously, the hydrogenation process of the DPB pellets is very complex and the kinetics of the hydrogen uptake of the DPB pellets, therefore, cannot be accurately described by a single stage geometrical diffusion model with a constant diffusion coefficient and a single activation energy. Consideration of the hydrogen uptake process by the DPB pellets at the atomic scale also leads to many questions and few answers (Fig. 10). The cartoon on the right-hand side of Fig. 10 depicts an exploded view of a Pd catalyst inside a DPB pellet. Each hydrogen molecule is split into two hydrogen atoms upon adsorbing on the Pd catalyst surface. These hydrogen atoms react readily with DPB molecules that touch the surface of the Pd catalyst to form a product layer of hydrogenated DPB. After the formation of this product layer, between the Pd catalyst surface and virgin DPB, how does the reaction continue? Would hydrogen leave the Pd catalyst surface and diffuse as atomic hydrogen through the thickening layer of hydrogenated DPB product to continue the reaction? Computational modeling suggests that the energy of direct desorption of a H radical from the Pd surface is prohibitively large,  $\sim 254$  kJ/mol.<sup>7</sup> However, there is experimental evidence in the literature to support the diffusion of atomic hydrogen on macroscopic scale away from the Pd catalyst surface when the Pd catalysts sits on a graphite substrate.<sup>8</sup> In the case of DPB pellets, the Pd catalysts are on a carbon support which is not graphitic in nature but more like amorphous carbon. Amorphous carbon does contain isolated local graphitic domains, but does not have a graphite structure on a large scale. So, the ability of hydrogen atoms to leave the Pd catalyst sites to react with DPB

molecules at far distance is greatly diminished in the DPB pellet structure. There is also a possibility that hydrogen radicals can hop through the hydrogen bonds in the hydrogenated DPB structures to react with far away DPB molecules, but a thorough study on this subject is still lacking in the literature.<sup>7</sup> Another question is whether the DPB molecules far away from the Pd catalysts can diffuse toward the Pd surface to capture hydrogen radicals. This is a real possibility given the liquid like nature of the DPB pellets during much of the hydrogenation process (see Fig. 5). All of these proposed mechanisms involve diffusion, raising the question of whether the diffusing species (hydrogen radicals and/or DPB molecules) strictly follows a one, two or three dimensional diffusion profile. The left-hand side cartoon in Fig. 10 illustrates this point. The DPB pellet contains 25 wt% catalyst (5 wt% Pd on carbon support). Since the average size of the Pd catalyst particle is on the order of nanometer scale, the average inter-particle distance is on the order of a few micrometers. The average thickness of the DPB layer on top of this structure of scattered Pd particles on carbon is also on the order of a few micrometers. The initial diffusion of hydrogen radicals away from the Pd surface (if at all possible) along the carbon surface have a two dimensional nature (actually three dimensional nature if the curvature of the carbon surface is taken into account). The diffusion of DPB molecules toward the Pd catalysts should have a three dimensional nature in the vicinity of the catalyst. A few micrometers away from the nanometer-scale Pd catalysts, the diffusion of DPB molecules toward the Pd should be more or less one dimensional in nature. At high levels of hydrogenation (images in the right column of Fig. 5), the diffusion of molecular hydrogen through the partially hydrogenated DPB liquid to reach the Pd catalysts only adds more complexity to the picture.

In order to circumvent the difficulties associated with what would be a very complicated atomistic or microscopic model, a semi-empirical kinetic model based on the general properties of gaseous diffusion into a solid (or liquid) was instead developed. A general property of all isothermal, isobaric processes in which the diffusion and incorporation of a gas into a solid (or liquid) is the rate limiting step can be written mathematically as:

$$P_1 t_1 = P_2 t_2 \quad \text{for } T_1 = T_2 = T \quad (5)$$

The mathematical proof of equation (5) can be found in Appendix A. The implication of equation (5) is that if it takes a time  $t_1$  at a constant pressure  $P_1$  to reach a certain conversion level (hydrogenation percentage or weight gain as in the case of this report), then it takes a time  $t_2$  at a constant but lower pressure  $P_2$  to reach the same conversion level such that  $t_2$  can be deduced from  $t_1$ ,  $P_1$  and  $P_2$ , given that the temperature  $T_1$  in the experiment with pressure  $P_1$  is the same as the temperature  $T_2$  in the experiment with pressure  $P_2$ . Previously reported experiments with hydrogen uptake in 1, 4-bis(phenylethynyl)benzene, also called DEB, mixed with carbon-supported Pd in a slab geometry confirmed that the diffusion of molecular hydrogen through the hydrogenated product layer to the virgin DEB compound material inside as the rate limiting step for the process.<sup>3</sup> Despite their different chemical formulae and physical properties (higher melting point and lower vapor pressure for DEB), DPB and DEB are in the same family of organic hydrogen getters, and the percentage of carbon-supported Pd catalyst in the DEB compound is the same as that for the DPB pellets. It is, therefore, expected that the diffusion of molecular hydrogen through the hydrogenated product layer to the virgin



DPB sites is also the rate limiting step for hydrogen uptake process in DPB pellets and that equation (5) is applicable.

In Fig. 11(a), the scatter in the maximum gettering capacities (or maximum hydrogenation percentage after correction for product volatility) of 10 DPB pellets is presented. It is noted that even though the average composition of DPB pellets is 75 wt% DPB and 25 wt% catalyst (5 wt% Pd on carbon support), the composition of individual DPB pellets vary somewhat from the nominal composition. Consequently, the observed scatter in the maximum gettering capacities of these 10 DPB pellets is likely a combination of intrinsic experimental error and the variation in the nominal composition of DPB pellets. In Fig. 11(b), the gray shadow represents the prediction of what the plot of hydrogenation percentage vs. time curve should look like for an isothermal (294 K) isobaric (10% H<sub>2</sub> + 90% He at one atmosphere) hydrogen uptake experiment by DPB pellets based on relationship (5) and the experimental data obtained using a gas mixture of 18% H<sub>2</sub> + 82% at one atmosphere. The spread in the time scale (~ 35 % error bar) of the gray shadow represents the typical scatter in experimental data obtained under similar conditions due to the non-uniformity of the pellets. The two dark solid lines in Fig. 11(b) are actual plots of the hydrogenation percentage vs. time for two experiments carried out in an isothermal (294 K), isobaric (10% H<sub>2</sub> + 90% He at one atmosphere) environment. Fig. 11(b) suggests that, within the observed scatter in data, hydrogen uptake data obtained at a higher hydrogen partial pressure (shorter experimental time) can be used to predict hydrogen uptake process at a lower hydrogen partial pressure using equation (5), provided that the temperature in the high pressure experiment is the same as that intended for the low pressure prediction.

In general, the hydrogen partial pressure in a real device is not constant over a long period of time. However, if the unit of time is chosen to be very small, such as one second, then during each one second time interval, the condition of constant pressure can be practically assumed and the use of equation (5) during that one second time interval is justified. The net hydrogen partial pressure in a device as a function of time can then be predicted numerically using:

$$P(t, \alpha) = P(t - \Delta t, \alpha - \Delta \alpha) + P_D'(t) \Delta t - \left( \frac{NRT}{VM_{H_2}} \right) \times \left\{ \frac{P(t - \Delta t, \alpha - \Delta \alpha)}{P_E} W_E'(\alpha) - \left[ W_L'(\alpha) \frac{P_{equi}(T)}{P_{equi}(294K)} \right] \frac{P_{equi}(T) - P_a(t - \Delta t, \alpha - \Delta \alpha)}{P_{equi}(T)} \right\} \Delta t \quad (6)$$

The derivation of equation (6) is found in APPENDIX B. In equation (6),  $P(t, \alpha)$  is the net hydrogen pressure in the device at time  $t$ . Note that  $P$  is a function of both time and the average hydrogenation percentage or consumption level of the DPB getter pellets,  $\alpha$ .  $P(t - \Delta t, \alpha - \Delta \alpha)$  is the net hydrogen partial pressure in the device at time  $(t - \Delta t)$  when the consumption level of the DPB pellet is  $\alpha - \Delta \alpha$ . In this work, equation (6) is solved numerically with a Fortran program and  $\Delta t$  is taken to be one second.  $P_D'(t)$  is the rate of hydrogen pressure increase, generated by all processes inside the device without any DPB getter, at time  $t$ . For the situations considered here,  $P_D$  is strictly a constant or only a function of time. The third term on the right-hand side of equation (6) represents the rate of hydrogen pressure decrease due to the scavenging action of the DPB getter pellets. Here,  $N$ ,  $R$ ,  $V$  and  $M_{H_2}$  stand for the number of DPB pellets employed in the device, molar gas constant, the free volume of the device, and molecular weight of hydrogen (2 g/mol), respectively.  $P_E$  is the hydrogen partial pressure employed in the isothermal,

isobaric experiment at higher pressure to obtain the plot of the H<sub>2</sub> uptake rate of one DPB getter pellet vs. the percentage hydrogenation,  $W'_E(\alpha)$  [see Fig. 9(b) at T = 294 K].

$W'_L(\alpha)$  is the experimentally obtained rate of weight loss of just one DPB pellet as a function of  $\alpha$  at 294 K (see Fig. 8),  $P_{equi}(T)$  is the equilibrium vapor pressure of the hydrogenated product at temperature  $T$ , and  $P_a(t - \Delta t, \alpha - \Delta\alpha)$  is the actual vapor pressure of the hydrogenated product in the device at time  $t - \Delta t$  and hydrogenation level  $\alpha - \Delta\alpha$ . At any given temperature, the performance of the DPB getter pellets, as described by equation (6), depends on the consumed getter capacity level, the instantaneous hydrogen partial pressure, the number of DPB getter pellets, and the free volume of the device. Note that since  $P_E$ ,  $W'_E(\alpha)$ , and  $W'_L(\alpha)$  were experimentally obtained, the hydrogen pressure buildup prediction equation (6) is semi-empirical in nature.

The use of equation (6) to obtain the hydrogen partial pressure evolution in a device is illustrated in Fig. 12. In Fig. 12(a), the experimentally measured hydrogen pressure buildup vs. time curve for a vessel having a free volume of 700 cc (or cubic centimeters), containing 20 DPB pellets at 294 K and subjected to a constant hydrogen input rate of 0.043 sccm is presented by the dark solid line. The light dashed line in the same figure represents the linear hydrogen pressure buildup curve resulting from a constant hydrogen input rate of 0.043 sccm in the same vessel under the same situation, but without any DPB getter pellet inside. Also in the same figure, the dark dashed line is the predictive modeling of what the hydrogen pressure buildup in the system is expected to look like from the use of equation (6) and isothermal isobaric data at higher hydrogen partial pressure presented in Fig. 9(b). Fig. 12(b) shows a similar situation to that in Fig. 12(a) but with a vessel having a free volume of only 522.3 cc and a constant hydrogen

input rate of 0.034 sccm. The discrepancy between the semi-kinetic prediction model and experimental hydrogen pressure buildup data is attributed to the non-uniformity of the DPB pellets and experimental errors in both the hydrogen pressure buildup experiments and the weight change experimental data employed in the semi-kinetic prediction model. From Fig. 12, it is observed that the DPB getter pellets' performance continually drops with increasing consumed capacity as expected for a gas-solid diffusion process. However, near the end life of the DPB getter pellets, a surge in the hydrogen gettering rate due to the re-solidification of the heavily hydrogenated DPB molecules on the high surface area carbon support [see Fig. 9(b) at  $\geq 85\%$  hydrogenation level] causes the hydrogen pressure buildup in the device to drop significantly until very near the end of life of the getter pellets. From that point on, the hydrogen pressure rise in the device is solely a function of the hydrogen input rate which is linear in this report.

In Fig. 13(a) is shown the plot of the hydrogen uptake rate per pellet vs. corrected hydrogenation percentage curve for typical isobaric, isothermal hydrogen uptake experiments for DPB pellets at 303 K. The gas used in this experiment was fixed at 10 %  $H_2/He$  mix at a pressure of one atmosphere. Analogous to Fig. 12, in Fig. 13(b), the experimentally measured hydrogen pressure buildup vs. time curve for a vessel having a free volume of 466.5 cc, containing 10 DPB pellets at 303 K and subjected to a constant hydrogen input rate of 0.027 sccm is presented by the dark solid line. The light dashed line represents the linear hydrogen pressure buildup curve resulting from a constant hydrogen input rate of 0.027 sccm in the same vessel without any DPB getter pellet. The dark dashed line in Fig. 13(b) represents the predictive modeling of what the hydrogen pressure buildup in the system is expected to look like from the use of equation (6) and

the weight gain rate per pellet vs. corrected hydrogenation level curve obtained in an isothermal, isobaric experiment at high hydrogen pressure [Fig. 13(a)]. In general, the DPB getter pellets lose their effectiveness as their capacity decreases (evidenced by the increase in the hydrogen pressure buildup with time). This is qualitatively expected for all reactions involving the diffusion of gas molecules through a constantly increasing product layer. The dramatic drop in hydrogen pressure near the end of life of DPB pellets at 294 K (as observed in Fig. 12) was, however, not present at 303 K (see Fig. 13). This drop in the hydrogen pressure in the device near the end of life of the DPB getter pellets was attributed to the re-solidification of the getter pellets at a high hydrogenation percentage from a liquid like state at 294 K as described earlier on. The re-solidification of the DPB getter pellets into a semi-porous structure, seen in Fig. 7, at high hydrogenation levels at 294 K helps to increase the flow of molecular hydrogen to unreacted sites, and, thus, increases the hydrogen scavenging effects. But at 303 K, the getter pellets still looked partially liquefied at the end of the hydrogen uptake experiment, suggesting the lack of a complete re-solidification process and therefore the absence of a surge in the getter performance near the getter's end of life at a temperature just a few degrees above 294 K. Unfortunately, further in-depth studies into the liquefaction of DPB getter pellets upon hydrogenation and subsequent re-solidification at high hydrogenation levels as a function of temperature are beyond the scope of this work. Overall, even though the predictive models presented in Figs. 12 and 13 don't fit precisely the experimental hydrogen pressure rise data, they successfully exhibit the trends of the hydrogen pressure buildup and serve to give, on the order of magnitude, the quantitative hydrogen pressure buildup dependence on the getter pellets' consumed capacity. With

that in mind, this semi-empirical kinetic prediction model can be used to predict the hydrogen pressure buildup in many practical device applications. For example, in Fig. 14, the hydrogen pressure buildup over more than a decade in a device having a free volume of 1000 cc, containing 300 DPB pellets, and subjected to a constant hydrogen input rate of 100 standard cubic centimeters per year (sccy) is presented. In this plot, the solid line and the dashed line represent the hydrogen pressure in the same device at 294 K and 303 K, respectively. Within experimental errors, the hydrogen pressure buildup seems to grow really fast at both temperatures after about 33 % to 40 % consumed capacity. Even though the performance of the DPB getter does not reach its lowest level until beyond 60 % hydrogenation level [see Figs. 9(b) and 13(a)], it seems to be a safe practice to replace the DPB getter pellets after about 33 % to 40 % consumed capacity when the hydrogen pressure starts to increase rapidly.

## **CONCLUSION:**

The physical and chemical properties of DPB getter pellets during hydrogenation were examined. The hydrogen uptake kinetics of these getter pellets were measured with a thermogravimetric analyzer (TGA) under isothermal, isobaric conditions at higher hydrogen partial pressure. The kinetics obtained was then used to develop a semi-empirical model, based on gas diffusion into solids, to predict the hydrogen uptake under dynamic conditions and at lower hydrogen partial pressures. The predictive models were compared against independent experimental data on hydrogen pressure buildup in sealed systems containing DPB getter pellets and subjected to constant rates of hydrogen input. The equilibrium vapor pressures and volatility of the hydrogenated DPB products and

their effects on the hydrogen uptake kinetics were also included in the predictive models. Due to the non-uniformity in the composition of the DPB getter pellets and experimental errors, the hydrogen uptake predictive models developed here do not fit exactly the independent data against which the models were validated. The models, however, successfully serve to give, on the order of magnitude, the dependence of the performance of the DPB getter pellets on their consumed capacity level, the instantaneous hydrogen partial pressure, the number of DPB getter pellets, and the free volume of the device. This investigation also reveals that the DPB getter pellets' performance drops significantly at ambient temperatures after the consumption of ~ 33 % to 40 % of the gettering capacity and that the pellets should probably be considered for replacement at this point. Nevertheless, in most practical devices equipped with plenty of DPB getter pellets, the hydrogen pressure buildup can be kept at safe levels for many years or even decades before this alarming point in the consumed capacity of the getters is reached. The methodology employed in developing the semi-empirical kinetic prediction approach presented here can also be used as a template for construction of kinetic prediction capability of gas uptake in other types of getters having complicated geometries and involving complex gas transport as long as the rate limiting step for the gas uptake is gas diffusion into a solid or liquid.

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#### **FIGURE CAPTIONS:**

**Fig. 1:** The chemical formulae for virgin DPB and fully hydrogenated DPB.

**Fig. 2:** The measured equilibrium vapor pressures of virgin DPB crystallites (solid circles), virgin DPB pellets with a formulation of 75 wt% DPB and 25 wt% Pd/C catalyst (open circles), and fully hydrogenated DPB crystallites (solid squares).

**Fig. 3:** The plot of  $\ln(P/P_o)$  vs.  $1/T$  for virgin DPB crystallites (solid circles), virgin DPB pellets with a formulation of 75 wt% DPB and 25 wt% Pd/C catalyst (open circles), and fully hydrogenated DPB crystallites (solid squares).

**Fig. 4:** SEM images of virgin DPB pellets at different magnification levels. The inset is an optical image of a few virgin DPB pellets. The bottom two SEM images show the



morphology at the outer surface of the virgin DPB pellets while the top two SEM images reveal the porosity (closed structure, not open porosity) of a fracture surface.

**Fig. 5:** The left column presents SEM images at the outer surface of a DPB pellet at around 25 wt% hydrogenation at different magnification levels, while the right column contains the optical images of another DPB pellet at around 75 wt% hydrogenation.

**Fig.6:** NMR investigation of the chemical structure of partially hydrogenation DPB.

**Fig. 7:** Optical (top right corner) and SEM (the rest) images of fully hydrogenated DPB pellets.

**Fig. 8:** A plot of the weight loss rate of hydrogenated DPB pellets as a function of the apparent hydrogenation percentage at room temperature (294 K) as recorded by the TGA.

**Fig. 9:** The hydrogenation percentage vs. time curve (a) and the weight gain rate per pellet vs. corrected hydrogenation percentage curve (b) for a typical experiment with DPB pellets at 294 K in an isobaric environment of one atmosphere (10 % H<sub>2</sub> + 90 % He) are presented.

**Fig. 10:** Cartoons illustrating the complexity involved in the uptake of hydrogen by DPB pellets at the microscopic and/or atomic levels.

**Fig. 11:** (a) the scatter in the maximum gettering capacities of 10 DPB pellets due to sample to sample variation in composition and (b) the level of agreement between actual isothermal, isobaric hydrogen uptake data at a H<sub>2</sub> partial pressure of 10,133 Pa and predicted uptake at 10,133 Pa from data at a H<sub>2</sub> partial pressure of 18,239 Pa at 294 K.

**Fig. 12:** Hydrogen pressure buildup without DPB getter pellets (light dashed lines) and with 20 DPB getter pellets (dark solid lines) at 294 K under a constant hydrogen input rate of 0.043 sccm in a 700 cc vacuum vessel (a) and under a constant hydrogen input

rate of 0.034 sccm in a 522.3 cc vacuum vessel(b). The dark dashed lines represent the hydrogen pressure rise as predicted by the semi-empirical kinetic predictive models described in equation (6).

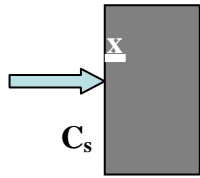
**Fig. 13:** (a) The weight gain rate per pellet vs. corrected hydrogenation percentage curve for a typical experiment with DPB pellets at 303 K in an isobaric environment of one atmosphere (10 % H<sub>2</sub> + 90 % He); (b) Hydrogen pressure in a vacuum vessels having a free volume of 466.5 cc without DPB getter pellets (light dashed lines) and with 10 DPB getter pellets (dark solid lines) at 303 K under a constant hydrogen input rate of 0.027 sccm. The dark dashed line represents the hydrogen pressure rise as predicted by the semi-empirical kinetic predictive model described in equation (6).

**Fig. 14:** Hydrogen pressure in a device having a free volume of 1000 cc, containing 300 DPB pellets, and subjected to a constant hydrogen input rate of 100 sccy.

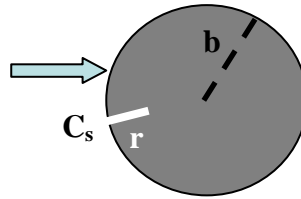
## **APPENDIX A:**

**Proof of  $P_1 t_1 = P_2 t_2$  at the same value of conversion level and temperature for isothermal isobaric processes involving the diffusion and incorporation of a gas into a solid (or similarly in the case of liquid) as the rate limiting step.**

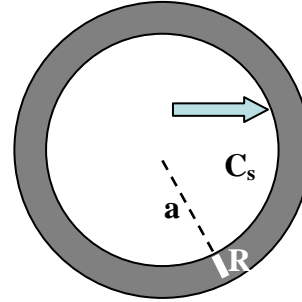
**Part I: The diffusion length vs. time curve is independent of surface curvature.**



**Diffusion into a slab**



**Radial diffusion into a circular cylinder**



**Diffusion out of a hollow sphere**

For Diffusion into a slab (one dimensional or 1D):

$$\text{From Fick's law of diffusion: } J = -D \nabla C = -\frac{DC_s}{x} \quad (\text{Ia})$$

Here,  $J$  is the diffusion flux,  $D$  is the diffusion coefficient, and  $C$  is the concentration of the diffusing species.  $C_s$  and  $x$  are the concentration of the diffusing gas at the surface of the slab facing the gas flow and the diffusing length, respectively.

Taking the point of view that diffusion involves the incorporation of the gaseous

$$\text{molecules into the slab matrix, } J \text{ can also be written as: } J = -\frac{1}{A} \frac{1}{m} \left( \rho A \frac{dx}{dt} \right) \quad (\text{IIa})$$

Here,  $A$  is the surface area of the slab which is perpendicular to the flow of gas and  $\rho$  is the density of the diffusing gas in the reacted layer. The mass of each molecule in the diffusing gas is labeled as  $m$ .

$$\text{Equate (Ia) and (IIa) to obtain: } x = \sqrt{2DC_s \frac{m}{\rho} t} \quad (\text{IIIa})$$

For radial diffusion into a right circular cylinder (two dimensional or 2D):

Analogous to the case of gaseous diffusion into a slab:

$$J = -\frac{DC_s}{r} = -\frac{1}{2\pi(b-r)h} \frac{1}{m} \frac{\partial W_r}{\partial t} \quad (\text{Ib})$$

Here,  $r$ ,  $b$ , and  $h$  are the radial diffusion length, the radius, and the height of the right circular cylinder, respectively.  $W_r$  is the weight gain due to the incorporation of the gas molecules into the reacted layer at the diffusion length  $r$ , and  $\frac{\partial W_r}{\partial t}$  is the partial derivative of the weight gain with respect to time. Note that  $W_r$  is a function of both  $r$  and  $t$ .

$$\text{But, } \frac{\partial W_r}{\partial t} = \rho \frac{\partial V_r}{\partial t} = \rho \frac{\partial V_r}{\partial r} \frac{\partial r}{\partial t} = \rho \left[ 2\pi(b-r)h \frac{\partial r}{\partial t} \right] \quad (\text{IIb})$$

In equation (IIb),  $V_r$  is the volume of the reacted product layer.

$$\text{Equate (Ib) and (IIb) to obtain: } r = \sqrt{2DC_s \frac{m}{\rho} t} \quad (\text{IIIb})$$

For diffusion out of a hollow sphere (three dimensional or 3D):

Analogous to the case above:

$$J = -\frac{DC_s}{R} = -\frac{1}{4\pi(a+R)^2} \frac{1}{m} \frac{\partial W_R}{\partial t} \quad (\text{Ic})$$

In equation (Ic),  $a$  is the inner radius of the hollow sphere while  $R$  and  $W_R$  are the radial diffusion length and the weight gain due to the incorporation of the gas molecules into the reacted layer at  $R$ . Note that  $W_R$  is a function of both  $R$  and  $t$ .

$$\text{But, } \frac{dW_R}{dt} = \rho \frac{\partial V_R}{\partial t} = \rho \frac{\partial V_R}{\partial R} \frac{\partial R}{\partial t} = \rho \left[ \frac{4}{3} \pi (3a^2 + 6aR + 3R^2) \frac{\partial R}{\partial t} \right] \quad (\text{IIc})$$

In equation (IIc),  $V_R$  is the volume of the reacted product layer.

$$\text{Equate (Ic) and (IIc) to obtain: } R = \sqrt{2DC_s \frac{m}{\rho} t} \quad (\text{IIIc})$$

The diffusion length vs. time curves for other diffusion geometries can also be analogously obtained. A comparison of equations (IIIa), (IIIb), and (IIIc) reveals that the values of the diffusion length as a function of time are identical and independent of the surface curvature or the 1D, 2D or 3D nature of the diffusion process if the concentration of the diffusing species at the surface perpendicular to the gas flow ( $C_s$ ) is the same.

**Part II: Proof of  $P_1 t_1 = P_2 t_2$  at the same value of conversion level and temperature for isothermal, isobaric processes involving the diffusion of a gas into a solid (or similarly in the case of liquid) as the rate limiting step.**

For Diffusion into a slab (1D):

A specific conversion level (or hydrogenation level as in the case of hydrogen uptake by getters) corresponds with a specific weight gain  $W = \rho A x$  due to the incorporation of the gaseous molecules into the host matrix. So, if the experiment is carried out at a constant pressure  $P_1$ , then from equation (IIIa):

$$W = \rho A \sqrt{2DC_s(T, P_1) \frac{m}{\rho} t_1} \quad (\text{IVa})$$

Similarly, if the experiment is done at a constant pressure  $P_2$ :

$$W = \rho A \sqrt{2DC_s(T, P_2) \frac{m}{\rho} t_2} \quad (\text{Va})$$

For gas diffusion into a solid, the concentration of the diffusing species at the surface of the sample perpendicular to the flow of gas is directly proportional to the partial pressure of the diffusing species so that:  $C_s(T, P_1) \propto P_1$  and  $C_s(T, P_2) \propto P_2$ . Substitute these values into equations (IVa) and (Va) and divide (IVa) by (Va) to see:

$$1 = \frac{\sqrt{P_1 t_1}}{\sqrt{P_2 t_2}} \quad (\text{VIa})$$

Or  $P_1 t_1 = P_2 t_2$  for a given weight gain at a given temperature.

For radial diffusion into a right circular cylinder (2D):

At a specific conversion level or weight gain  $W$ ,  $W = \rho V$  where  $V$  is the volume of the reacted product layer. If the experiment is performed at pressure  $P_1$ :

$$W = \rho h \pi \left[ b^2 - \{b - r(T, P_1, t_1)\}^2 \right] \quad (\text{IVb})$$

If the experiment is done at pressure  $P_2$ :

$$W = \rho h \pi \left[ b^2 - \{b - r(T, P_2, t_2)\}^2 \right] \quad (\text{Vb})$$

$$\text{From equations (IVb) and (Vb): } r(T, P_1, t_1) = r(T, P_2, t_2) \quad (\text{VIb})$$

For the same reason as in the case of diffusion into a slab:  $C_s(T, P_1) \propto P_1$  and

$C_s(T, P_2) \propto P_2$ . With this and equation (IIIb), the relationship (VIb) can be rearranged to

read:  $\sqrt{P_1 t_1} = \sqrt{P_2 t_2}$  or  $P_1 t_1 = P_2 t_2$  for a given weight gain at a given temperature.

For diffusion out of a hollow sphere (3D):

Perform analogous analysis as in the case of radial diffusion into a right circular cylinder

$$\text{to see: } W = \rho \frac{4}{3} \pi \left[ \{a + R(T, P_1, t_1)\}^3 - a^3 \right] = \rho \frac{4}{3} \pi \left[ \{a + R(T, P_2, t_2)\}^3 - a^3 \right]$$

So:  $R(T, P_1, t_1) = R(T, P_2, t_2)$  and  $P_1 t_1 = P_2 t_2$  for a given weight gain at a given temperature.

Analogous analysis can also be used to derive at the same conclusion for other geometries.

## **APPENDIX B:**

### **Derivation of equation (6).**

The hydrogen partial pressure in a device,  $P$ , is a function of both time,  $t$ , and the hydrogenation percentage or consumption level of the DPB pellets,  $\alpha$ , and can be written as:

$$P(t, \alpha) = P(t - \Delta t, \alpha - \Delta \alpha) + \Delta P_D - \Delta P_G \quad (\text{VII})$$

The meaning of equation (VII) is that the hydrogen partial pressure in the device,  $P(t, \alpha)$ , is simply equal the hydrogen partial pressure at an earlier time,  $t - \Delta t$ , when the consumption level of the getter pellets is  $\alpha - \Delta \alpha$ , plus the hydrogen pressure increase due to all hydrogen generating processes in the device ( $\Delta P_D$ ) during the time  $\Delta t$  minus the hydrogen pressure decrease due to the hydrogen scavenging effect of the DPB pellets ( $\Delta P_G$ ) during that same time interval.

If the free volume of a device is  $V$  and the mole of hydrogen captured by  $N$  pellets of DPB is  $n$ , then from the ideal gas law:

$$V \frac{\Delta P_G}{\Delta t} = RT \frac{\Delta n}{\Delta t} = \frac{RT}{M_{H_2}} \left( N \frac{\Delta W}{\Delta t} \right) \quad (\text{VIII})$$

In equation (VIII),  $R$  is the molar gas constant,  $M_{H_2}$  is the molecular weight of hydrogen,

$\frac{\Delta P_G}{\Delta t}$  is the rate of hydrogen pressure decrease due to the scavenging action of the DPB

getter pellets, and  $\frac{\Delta W}{\Delta t}$  is the rate of weight gain due to hydrogen uptake of just one DPB pellet.

If the temperature involving in two isothermal, isobaric hydrogen uptake experiments at pressure  $P_1$  and pressure  $P_2$  are the same, then at any specific weight gain  $W$  and from equation (5):

$$\frac{P_2}{P_1} = \frac{t_1}{t_2} = \frac{Wt_1}{Wt_2} = \frac{W/t_2}{W/t_1} \quad (\text{IX})$$

Realizing that, for isobaric experiments,  $P_2/P_1$  is just a constant at all values of  $W$ ,  $t_2$ , and  $t_1$ , equation (IX) can be rewritten as:

$$\frac{t_1}{t_2} = \frac{P_2}{P_1} = \frac{\Delta W / \Delta t_2}{\Delta W / \Delta t_1} \quad (\text{X})$$

Note that  $\Delta W / \Delta t_1$  is simply the rate of weight gain under the isothermal, isobaric condition at  $T$  and higher pressure  $P_1$  and can be relabeled as  $\Delta W_E / \Delta t$  if  $P_1$  is relabeled as  $P_E$ . Similarly,  $\Delta W / \Delta t_2$  is simply the rate of weight gain under the isothermal, isobaric condition at  $T$  and lower pressure  $P_2$  and can be relabeled as  $\Delta W / \Delta t$  if  $P_2$  is relabeled as  $P$ . With the above changes in symbols, equation (X) becomes:

$$\frac{\Delta W}{\Delta t} = \frac{P}{P_E} \frac{\Delta W_E}{\Delta t} \quad (\text{XI})$$

Substitute equation (XI) into equation (VIII) to see:

$$\frac{\Delta P_G}{\Delta t} = \frac{NRT}{VM_{H_2}} \frac{P}{P_E} \frac{\Delta W_E}{\Delta t} \quad (\text{XII})$$

Note that the hydrogen partial pressure  $P$  in a real device is not constant over a long period of time. However, if the unit of time is chosen to be very small, such as  $\Delta t = 1$  second, then during each  $\Delta t$  interval, the condition of constant pressure can be practically assumed and the use of equation (5) and equation (XII) during each  $\Delta t$  interval is justified. Also with  $\Delta t = 1$  second in a numerical calculation, the difference in  $P(t, \alpha)$  and  $P(t - \Delta t, \alpha - \Delta \alpha)$  is negligible and equation (XII) can be approximated by:

$$\frac{\Delta P_G}{\Delta t} \approx \frac{NRT}{VM_{H_2}} \frac{P(t - \Delta t, \alpha - \Delta \alpha)}{P_E} \frac{\Delta W_E}{\Delta t} \quad (\text{XIII})$$



Since  $\Delta W_E / \Delta t$  was obtained experimentally as a function of hydrogenation percentage  $\alpha$

[see Fig. 9(b), Fig.13(a) and Appendix C], it is logical to replace  $\frac{\Delta W_E}{\Delta t}$  with  $W'_E(\alpha)$  in

equation (XIII):

$$\frac{\Delta P_G}{\Delta t} \approx \frac{NRT}{VM_{H_2}} \frac{P(t - \Delta t, \alpha - \Delta \alpha)}{P_E} W'_E(\alpha) \quad (XIV)$$

Note that in this work, the hydrogen generation processes in the device,  $P_D$ , is

independent of the hydrogen pressure buildup in the system and of the hydrogenation

percentage of the DPB pellets ( $P'_D \equiv \frac{\Delta P_D}{\Delta t}$  is only a constant or a function of time).

Substitute equation (XIV) into equation (VII) to see:

$$P(t, \alpha) = P(t - \Delta t, \alpha - \Delta \alpha) + P'_D(t) \Delta t - \frac{NRT}{VM_{H_2}} \frac{P(t - \Delta t, \alpha - \Delta \alpha)}{P_E} W'_E(\alpha) \Delta t \quad (XV)$$

Due to the volatility of hydrogenated DPB, hydrogenated DPB vapor continues to build in the device until an equilibrium vapor pressure [see equation (2), Table I, Figs. 2 and 3]

is reached in the device. In order to properly account for this volatility,

$\frac{P(t - \Delta t, \alpha - \Delta \alpha)}{P_E} W'_E(\alpha)$  in equation (XV) needs to be modified to read:

$$\frac{P(t - \Delta t, \alpha - \Delta \alpha)}{P_E} W'_E(\alpha) - \left[ W'_L(\alpha) \frac{P_{equi}(T)}{P_{equi}(294K)} \right] \frac{P_{equi}(T) - P_a(t - \Delta t, \alpha - \Delta \alpha)}{P_{equi}(T)} \quad (XVI)$$

Here,  $W'_L(\alpha)$  is the experimentally obtained rate of weight loss of just one DPB pellet as a

function  $\alpha$  at 294K (see Fig. 8 and Appendix C),  $P_{equi}(T)$  is the equilibrium vapor

pressure of the hydrogenated product at temperature  $T$ , and  $P_a(t - \Delta t, \alpha - \Delta \alpha)$  is the actual

vapor pressure of the hydrogenated product in the device at time  $t - \Delta t$  and hydrogenation

level  $\alpha - \Delta\alpha$ . When  $P_a$  reaches its theoretical maximum which is the value of  $P_{equi}$ , the vaporization of the hydrogenated product stops and the second term in equation (XVI) vanishes thereafter.

$P_a$  can be obtained from:

$$P_a(t - \Delta t, \alpha - \Delta\alpha) = \left[ \frac{\sum_{i=1}^{(t-\Delta t)/\Delta t} W'_L(\alpha) \Delta t_i}{M_{hydrogenated\ DPB}} \right] \left( \frac{RT}{V} \right) \quad (XVII)$$

With the modification of  $W'_E$  presented in equation (XVI), equation (XV) becomes:

$$P(t, \alpha) = P(t - \Delta t, \alpha - \Delta\alpha) + P'_D(t) \Delta t - \left( \frac{NRT}{VM_{H_2}} \right) \times \left\{ \frac{P(t - \Delta t, \alpha - \Delta\alpha)}{P_E} W'_E(\alpha) - \left[ W'_L(\alpha) \frac{P_{equi}(T)}{P_{equi}(294K)} \right] \frac{P_{equi}(T) - P_a(t - \Delta t, \alpha - \Delta\alpha)}{P_{equi}(T)} \right\} \Delta t$$

This is equation (6) with  $\alpha$  determined by:

$$\alpha = 100 \left[ \frac{\sum_{i=1}^{t/\Delta t} \left\{ W'_E(\alpha) - \left[ W'_L(\alpha) \frac{P_{equi}(T)}{P_{equi}(294K)} \right] \frac{P_{equi}(T) - P_a(t - \Delta t, \alpha - \Delta\alpha)}{P_{equi}(T)} \right\} \Delta t_i}{0.75m_p} \right] \quad (XIX)$$

(4M<sub>H<sub>2</sub></sub> / M<sub>DPB</sub>)

In formula (XIX),  $m_p$  is the mass of one virgin DPB pellet which is roughly 0.020562g,  $M_{DPB}$  is the molecular weight of DPB which is 202g/mole,  $M_{Hy\ DPB}$  is the molecular weight of fully hydrogenated DPB, and  $M_{H_2}$  is the molar weight of hydrogen which is 2g/mole.

Note that  $\alpha$  as defined in equation (XIX) is the argument in the  $W'_E(\alpha)$  and  $W'_L(\alpha)$  formulae, and accounts for the dependence of the weight gain and weight loss in a device

with a dynamic hydrogen pressure on the volatility of the hydrogenated product. The absolute hydrogenation percentage of the DPB getter pellets in a dynamic hydrogen pressure situation,  $\alpha_a$  is simply given by:

$$\alpha_a = 100 \frac{\left[ \frac{\sum_{i=1}^{t/\Delta t} W'_E(\alpha) \Delta t_i}{0.75m_p} \right]}{(4M_{H_2} / M_{DPB})} \quad (XX)$$

## APPENDIX C:

Analytical expressions for  $W'_E$  vs.  $\alpha$  at 294K and 303K, and for  $W'_L$  vs.  $\alpha$  at 294K

### Mathematical fit of the weight loss rate vs. apparent hydrogenation percentage curve of Fig. 8

The weight loss rate vs. apparent hydrogenation percentage curve in Fig. 7 can be fitted with any suitable mathematical formulation. A combination of a log normal distribution and a polynomial in a double precision format (16 digits) is a suitable analog fit to such a curve and can be expressed as:

$$y = \frac{1}{60.0} \left\{ (1.821532826222945 \times 10^{-6}) \frac{\exp\left(-\frac{(\ln x - 2.894902118339475)^2}{2(0.3206153397880946)^2}\right)}{0.3206153397880946(\sqrt{2\pi})x} \right\} +$$

$$(3.209230033600553 \times 10^{-9}) + (8.894459295108791 \times 10^{-10})x +$$

$$(1.802929976313459 \times 10^{-10})x^2 - (7.142718159120020 \times 10^{-12})x^3 +$$

$$(8.754141192227882 \times 10^{-14})x^4 - (3.482304837056636 \times 10^{-16})x^5$$

where  $y$  represents the weight loss rate,  $W'_L$ , in unit of g/s at 294K and  $x$  is apparent hydrogenation percentage..

### **Mathematical fit of the weight gain rate vs. hydrogenation percentage curve at 294K**

#### **[Fig. 9(b)]**

Due to the peak around 85% hydrogenation, the curve should be broken into two parts for separate fittings. The portion of the curve up to 85% hydrogenation percentage can be fitted with a polynomial of 9<sup>th</sup> order as following:

$$y = (1.781749263701982e^{-5} - 4.35974684650211e^{-6}x + 4.867236167211415e^{-7}x^2 - 2.967803500300019e^{-8}x^3 + 1.094432541422219e^{-9}x^4 - 2.560257404971820e^{-11}x^5 + 3.830285181462341e^{-13}x^6 - 3.552048562863368e^{-15}x^7 + 1.859176702897421e^{-17}x^8 - 4.195181533490433e^{-20}x^9) \frac{1}{60.0}$$

where  $y$  is the weight gain rate,  $W_E'$ , in unit of gram per minute (g/min) and  $x$  is hydrogenation percentage [corrected or absolute hydrogenation percentage in the case of an isothermal, isobaric experiment as presented in Fig. 9(b), but an apparent hydrogenation percentage in the case of a dynamic hydrogen pressure situation like that in a device kinetic prediction].

The portion of the curve beyond 85% hydrogenation percentage can be fitted with a polynomial of 3<sup>th</sup> order as following:

$$y = 0.01308060344426399 - 0.0004459376177877662x + 5.061855532282121e^{-6}x^2 - 1.912834748097113e^{-8}x^3$$

with  $y$  and  $x$  defined as above.

### **Mathematical expression of the weight gain rate vs. hydrogenation percentage curve**

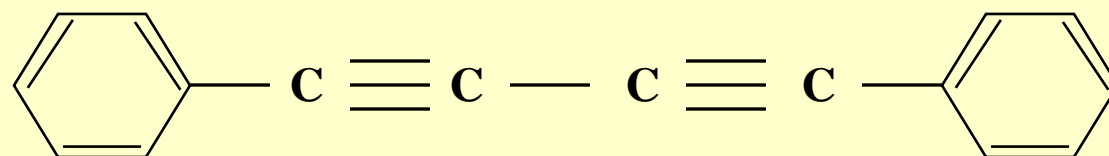
#### **at 303K [Fig. 13(a)]**

The curve can be satisfactorily fitted with a polynomial of 9<sup>th</sup> order as following:

$$y = 7.570930727541158e^{-6} - 1.866004587105619e^{-6}x + 2.348796534139313e^{-7}x^2 - 1.521736701486185e^{-8}x^3 + 5.601249720088819e^{-10}x^4 - 1.246256159712781e^{-11}x^5 + 1.711439625409121e^{-13}x^6 - 1.420023916007660e^{-15}x^7 + 6.530460222687018e^{-18}x^8 - 1.278537085586561e - 20x^9$$

With  $y$  and  $x$  defined as in the case at 294K.

**1, 4 – diphenylbutadiyne (virgin DPB)**



**1, 4 – diphenylbutane (hydrogenated DPB)**

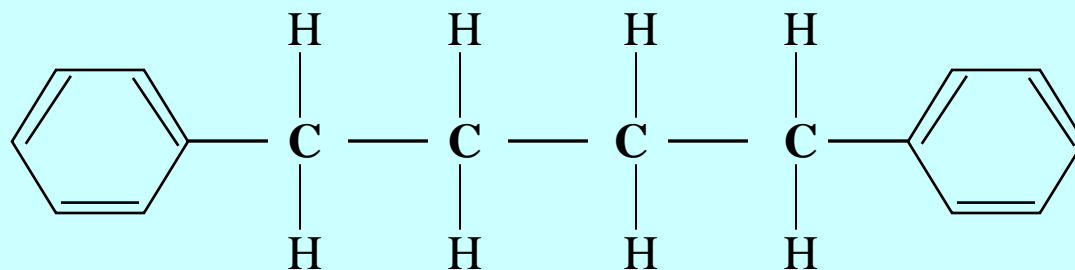


Fig. 1

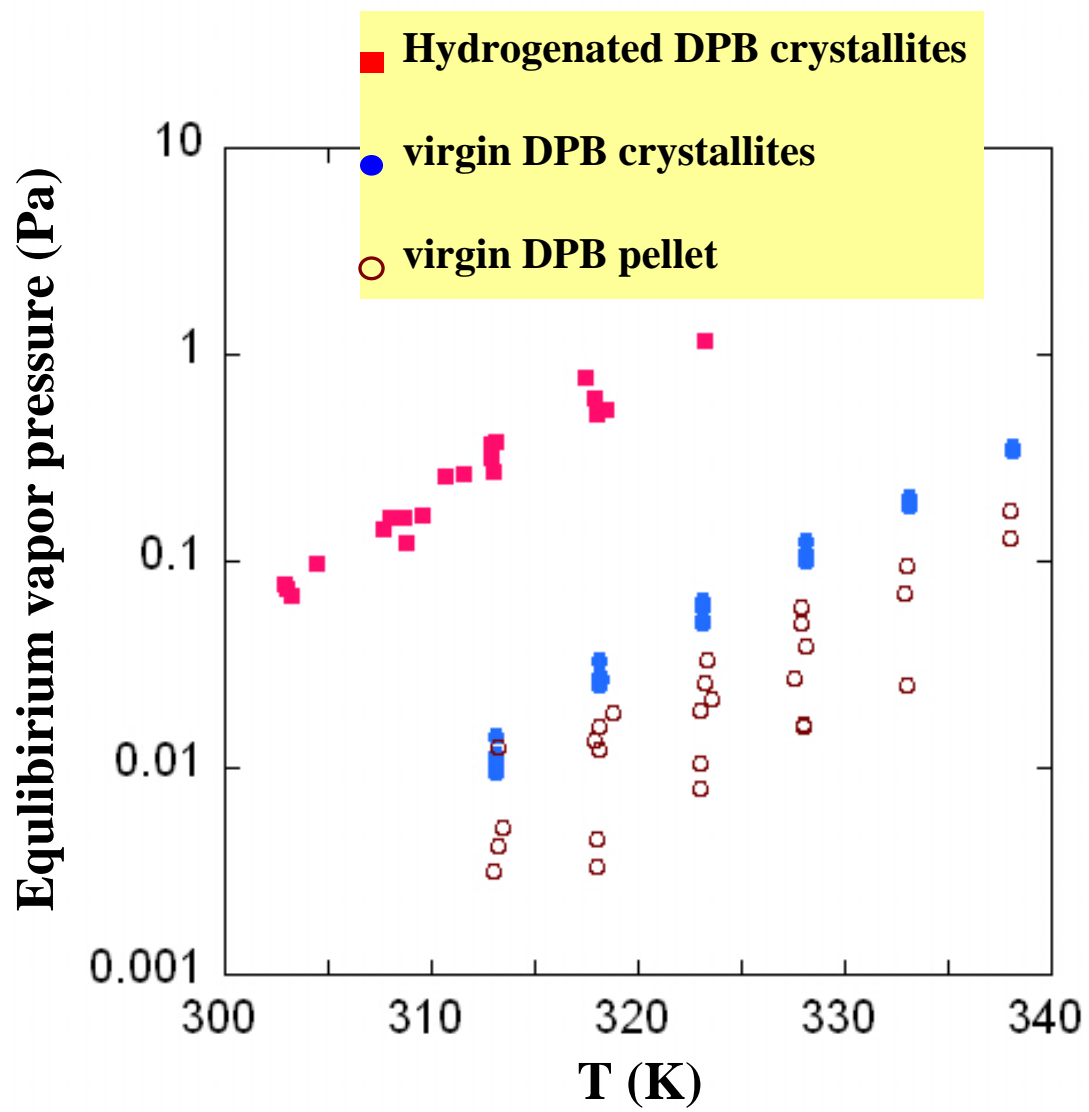


Fig. 2

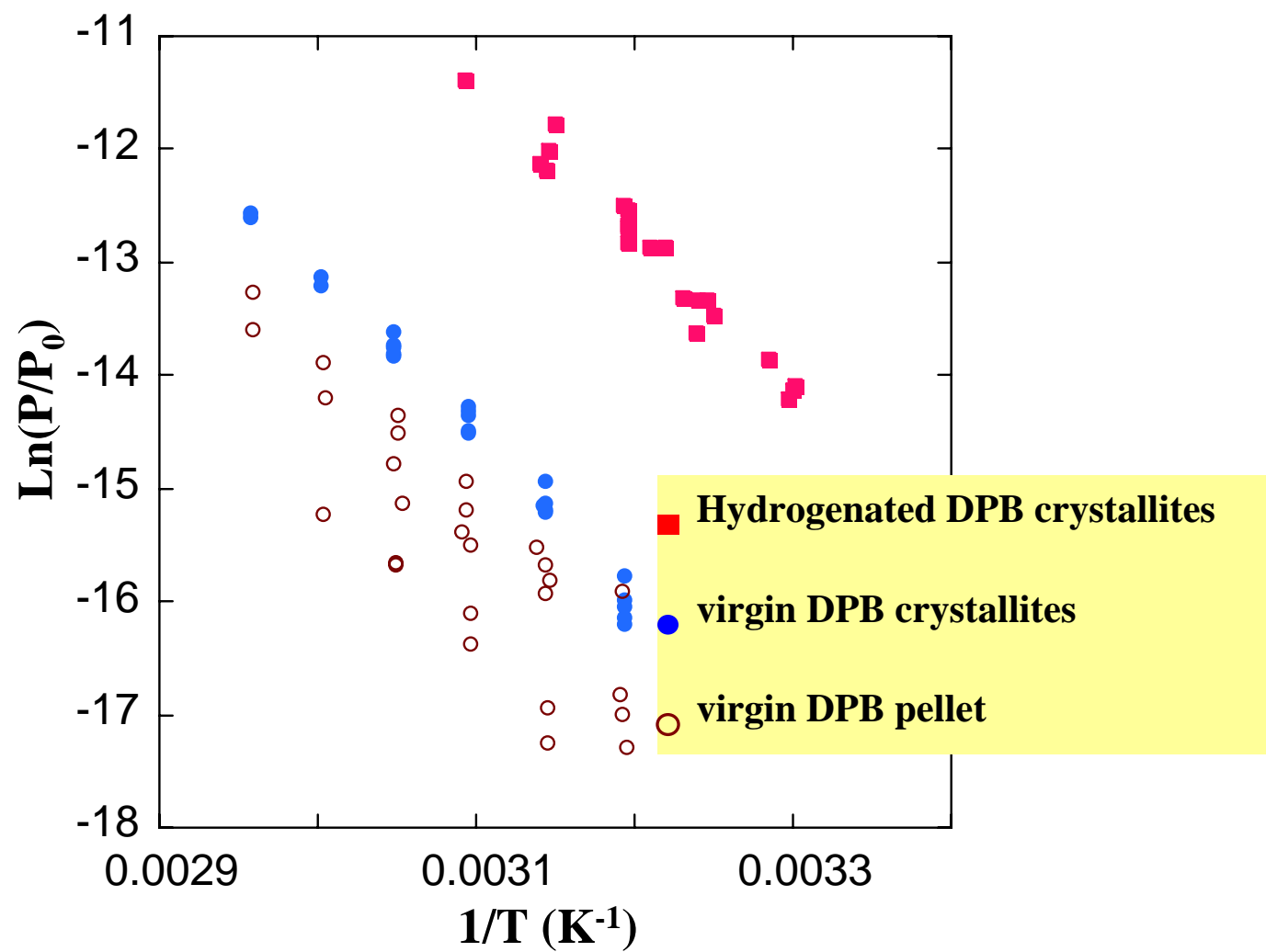


Fig. 3



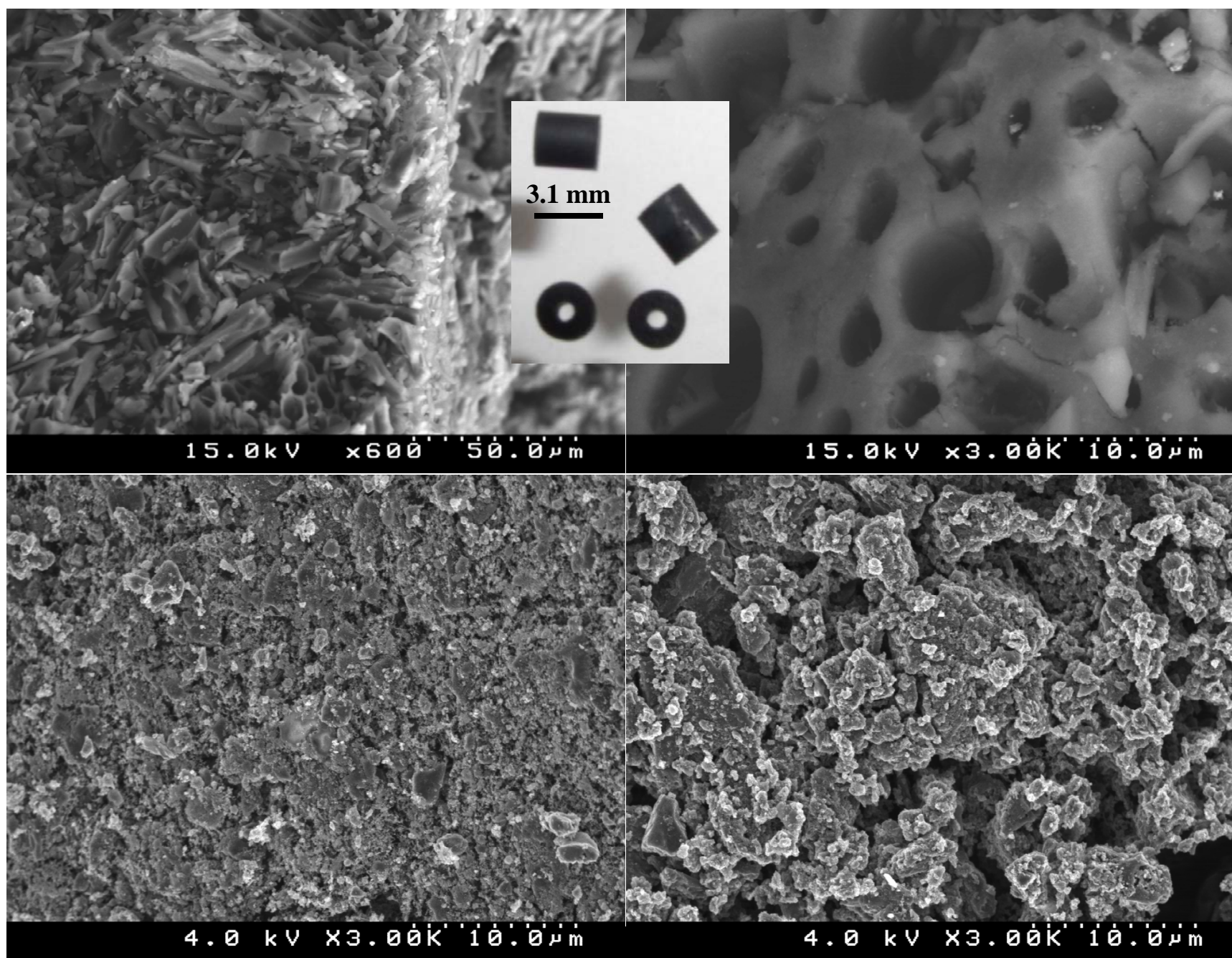
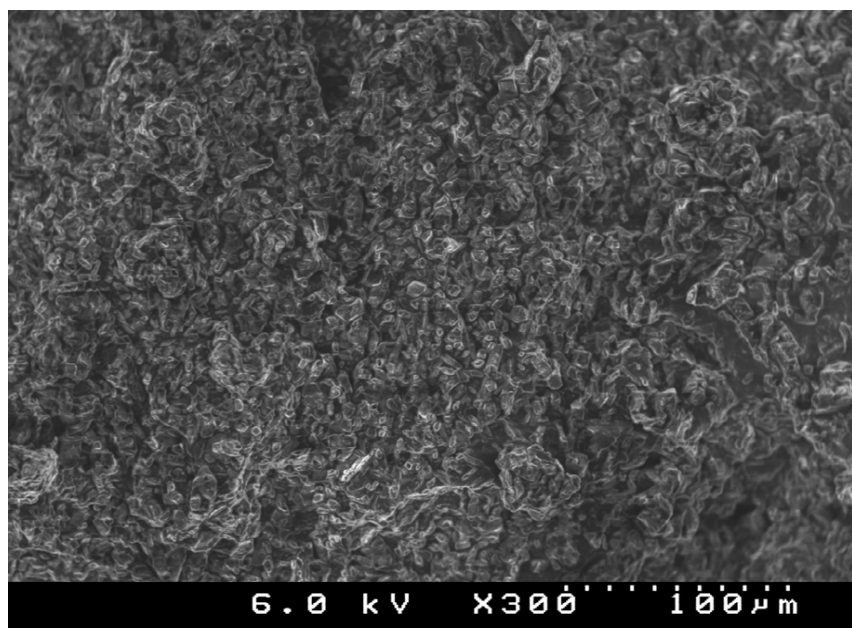
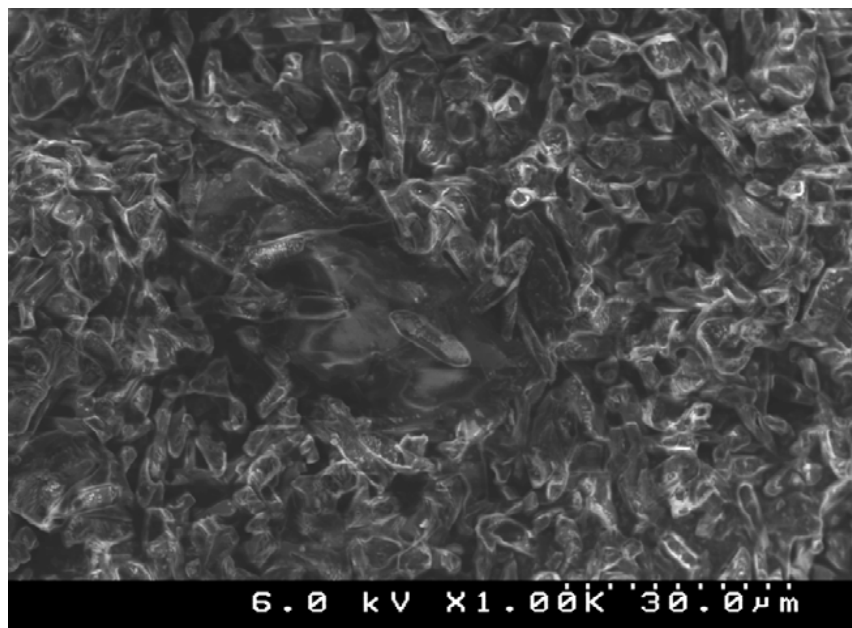


Fig. 4

## 25% hydrogenated pellet



## 75% Hydrogenation

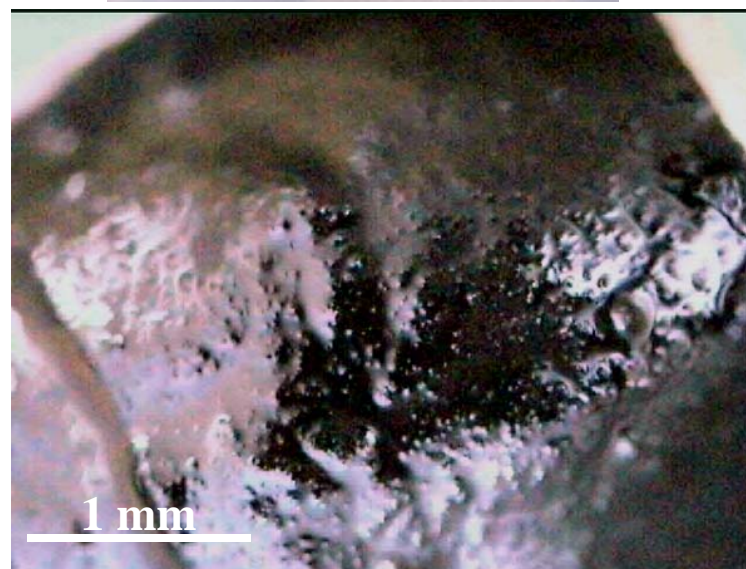
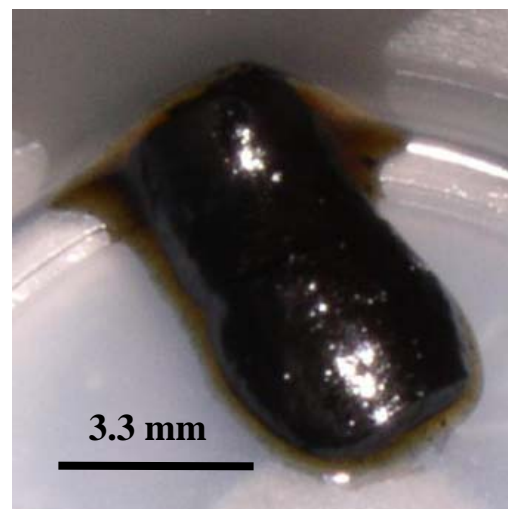
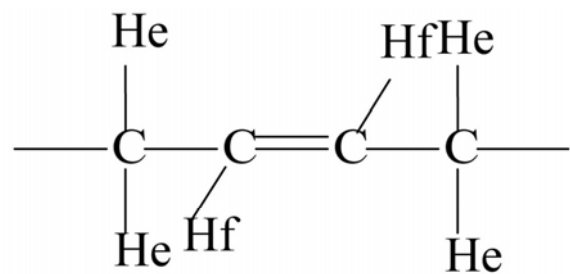


Fig. 5





or

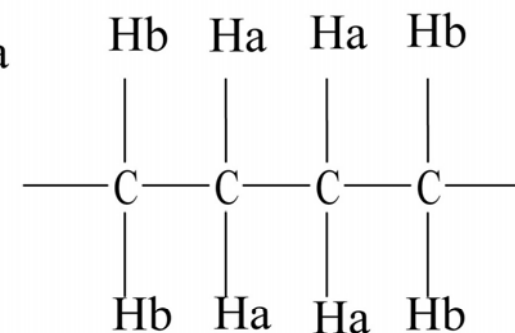
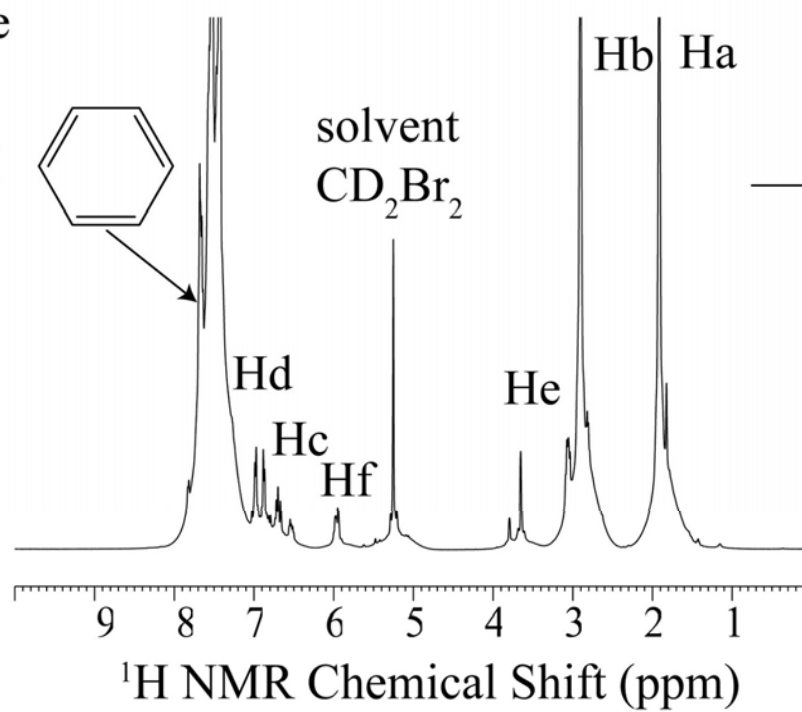
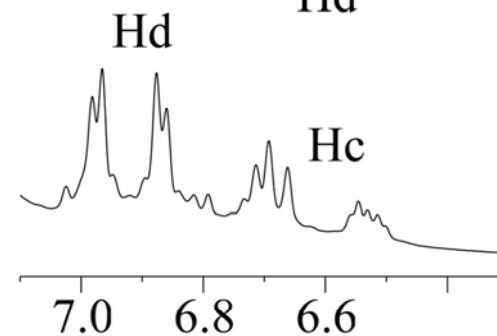
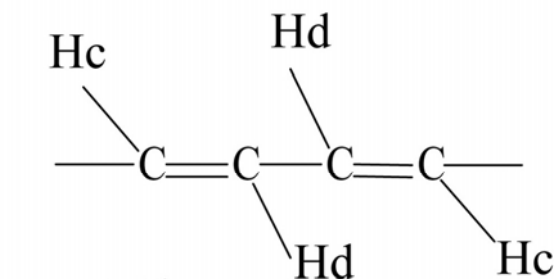
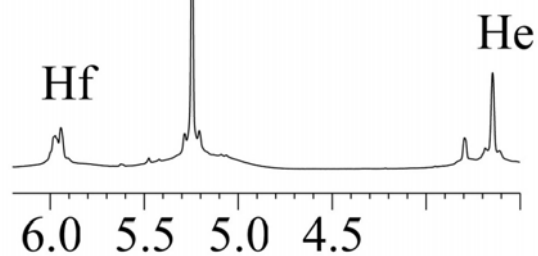
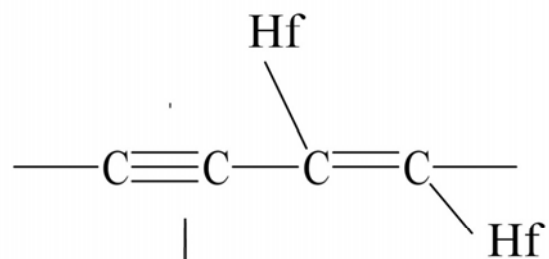


Fig. 6

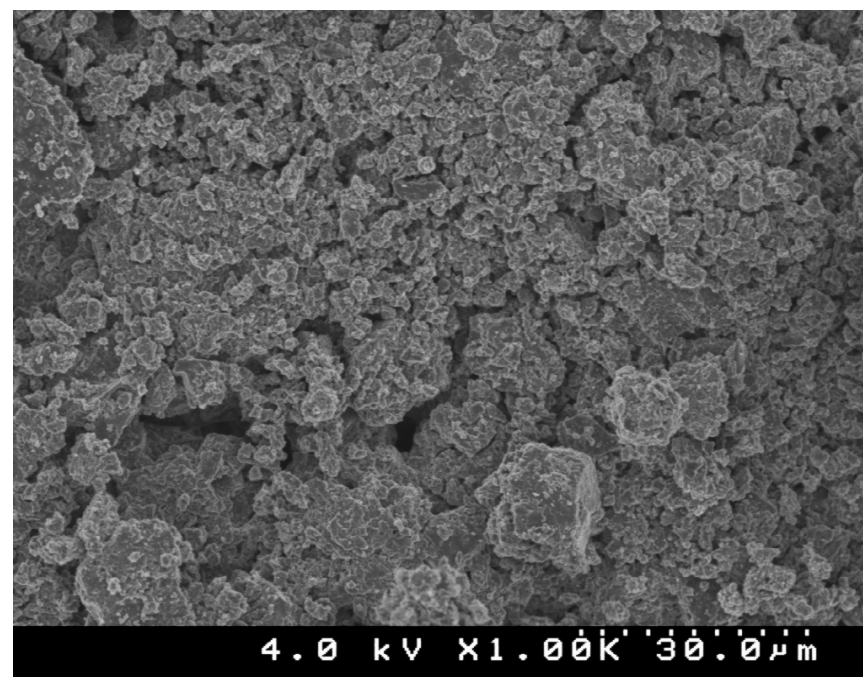
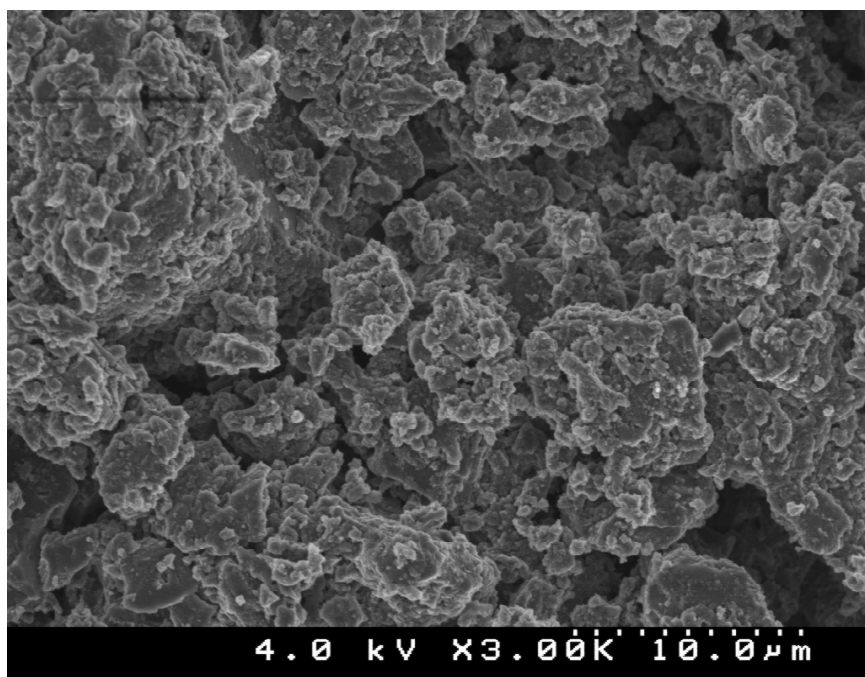
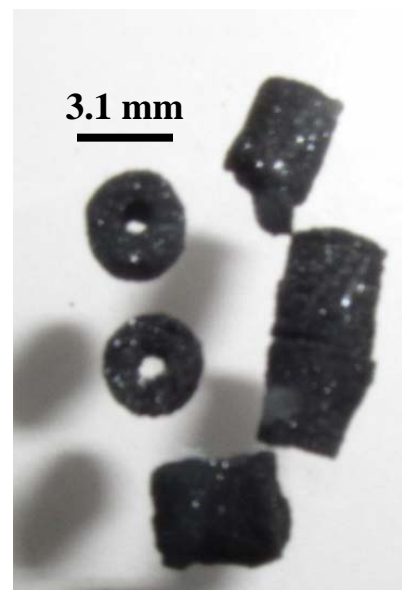
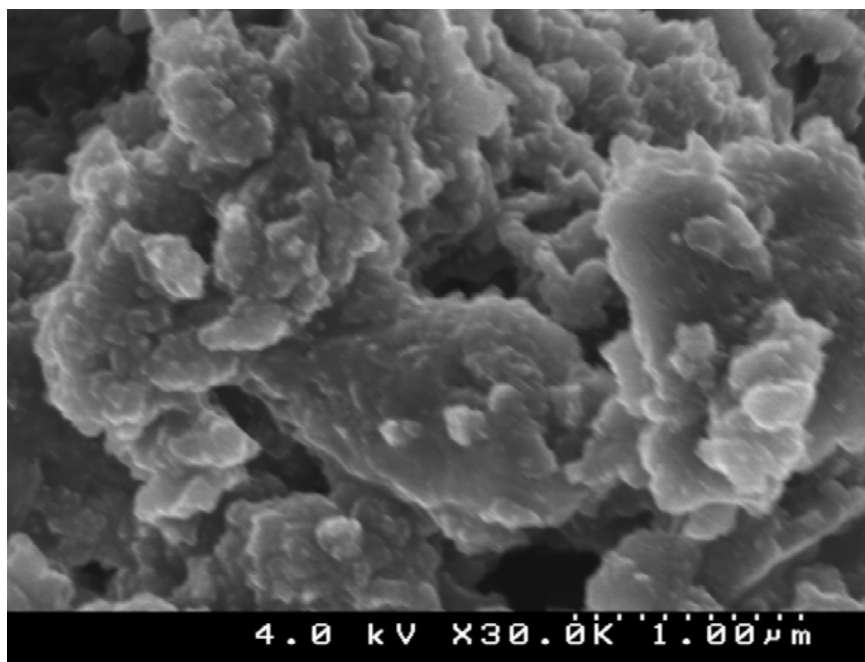


Fig. 7

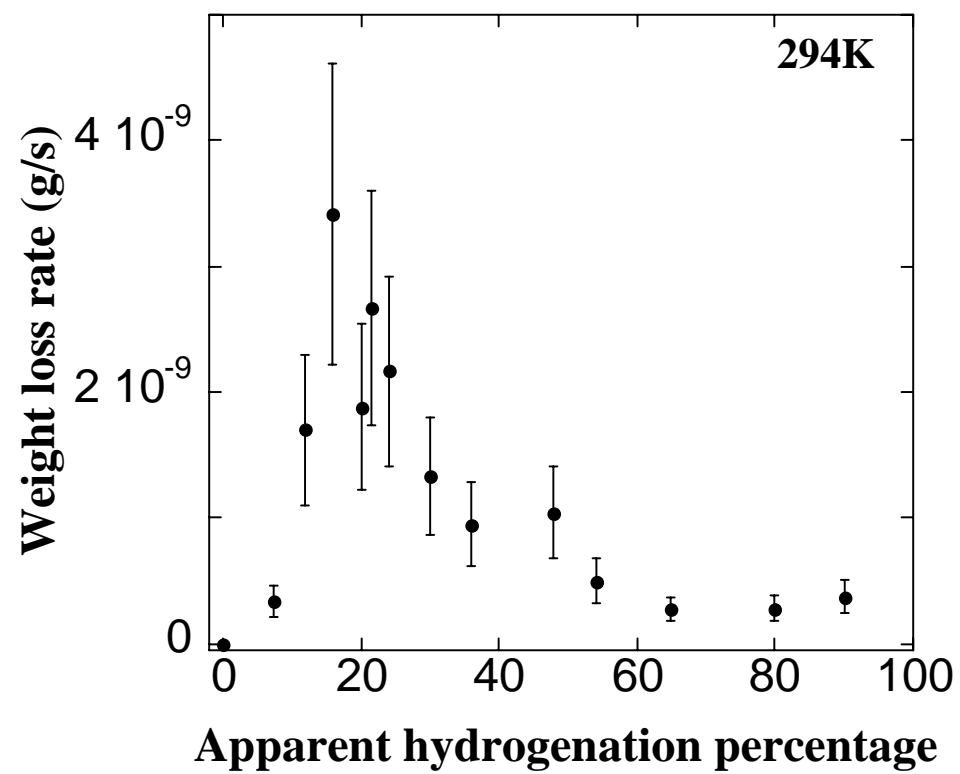


Fig. 8

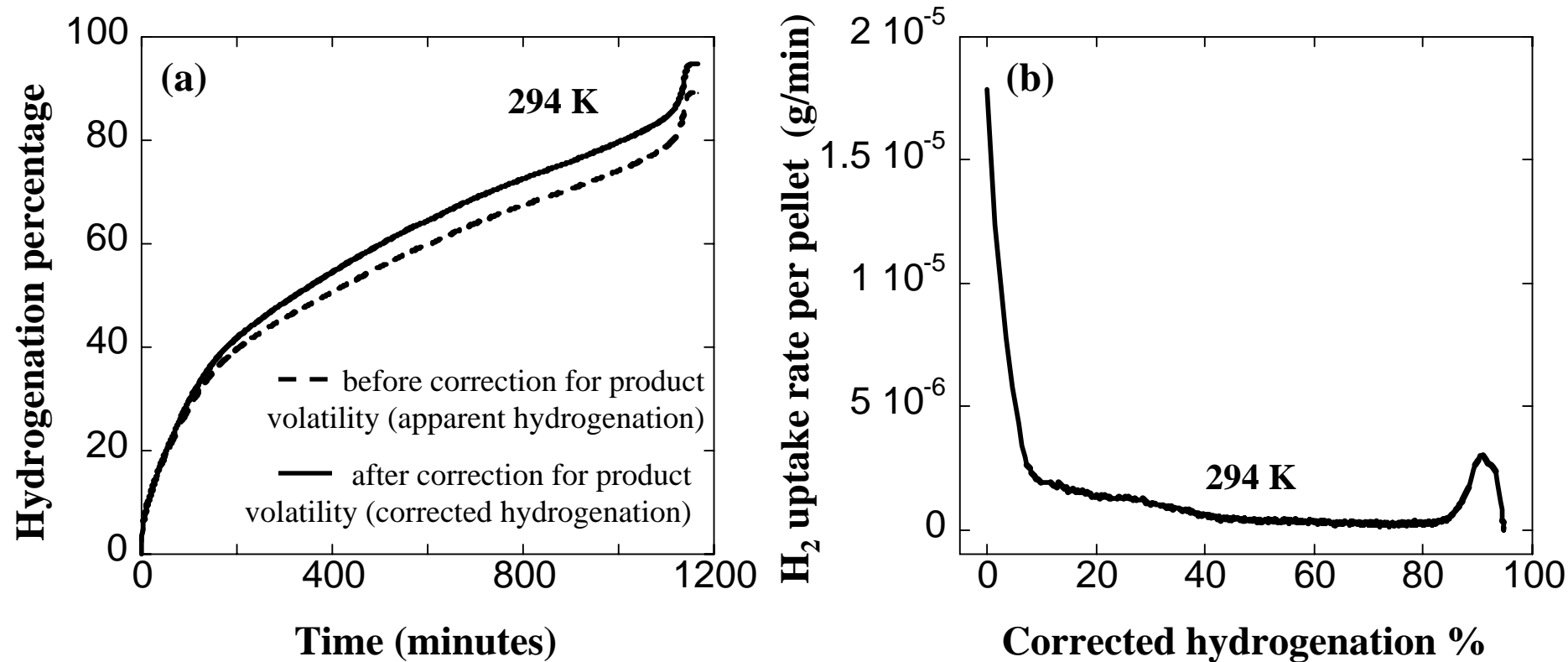


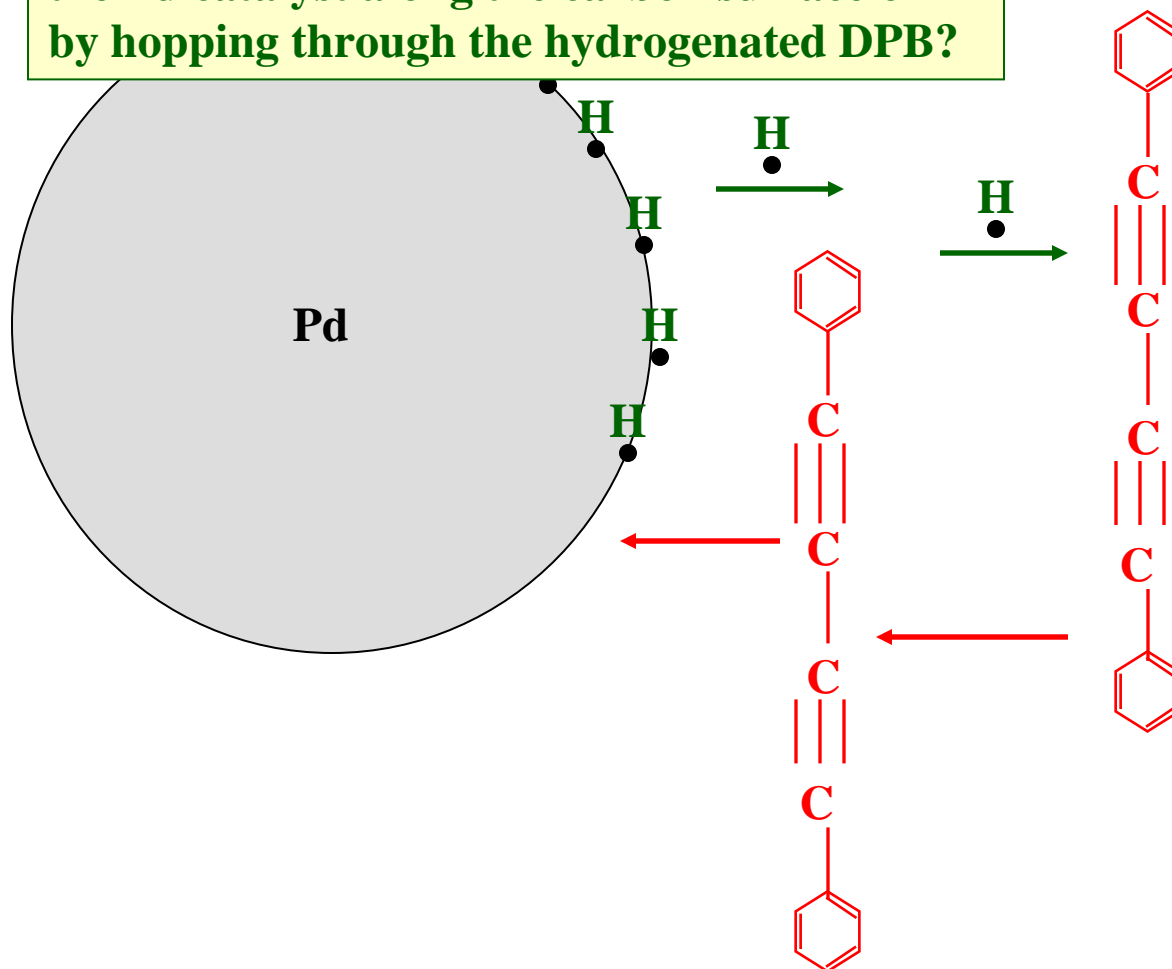
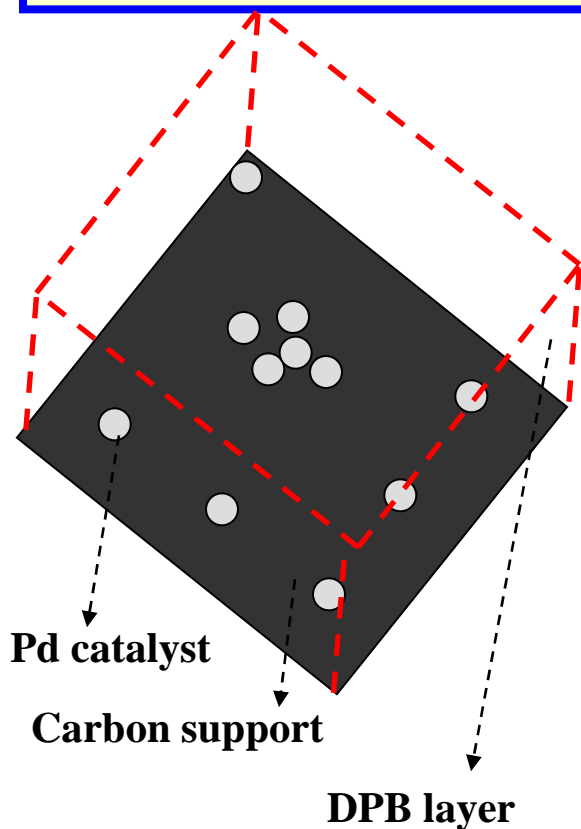
Fig. 9

Is the nature of the diffusion process 1D, 2D, 3D or a combination of these in different stages?

Molecular hydrogen diffusion through the partially hydrogenated DPB liquid adds more complexity to the picture.

## Some fundamental questions

Can the atomic hydrogen diffuse away from the Pd catalyst along the carbon surface or by hopping through the hydrogenated DPB?



Or do DPB molecules diffuse toward the Pd surfaces?

Fig. 10

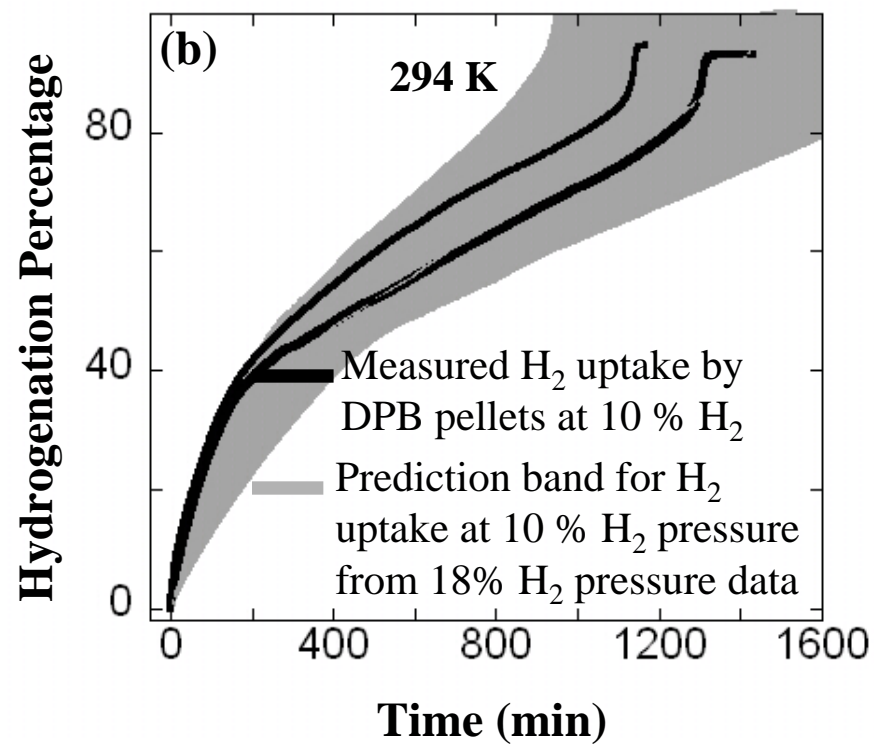
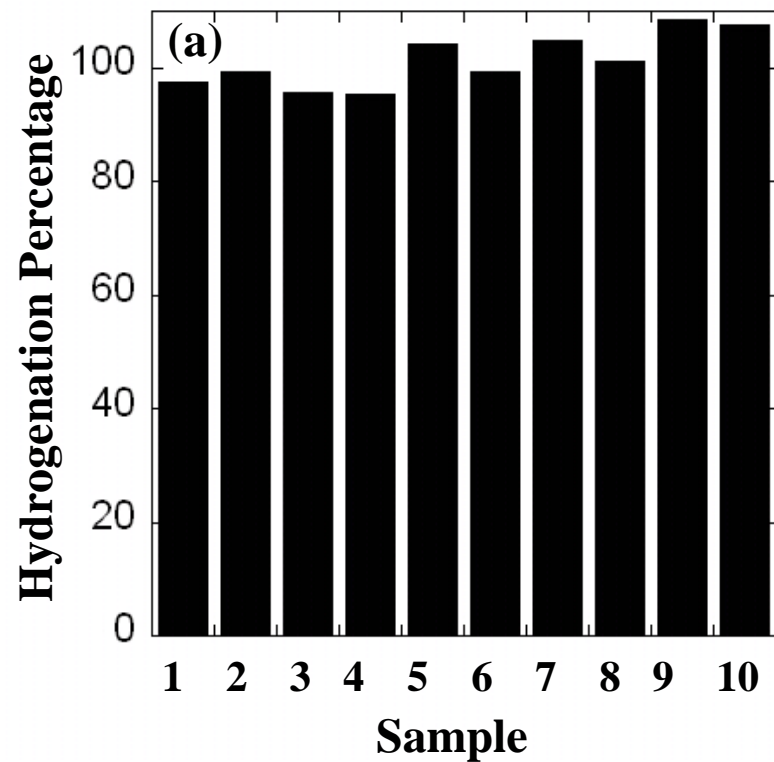


Fig. 11



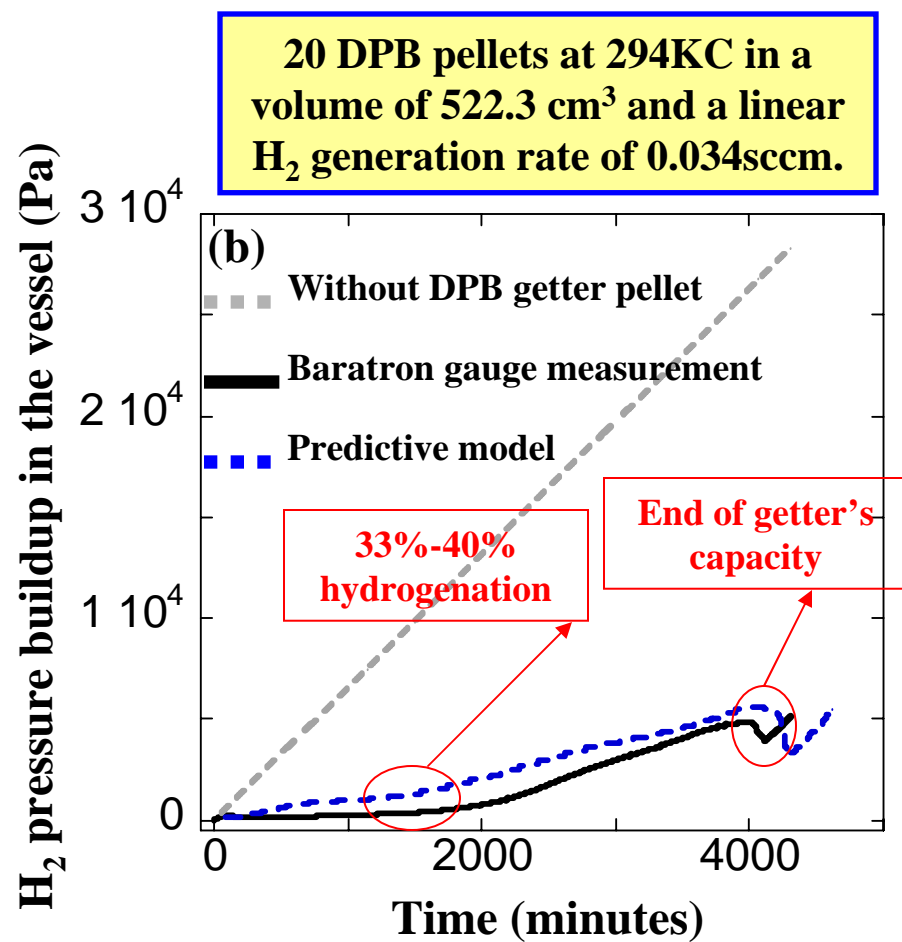
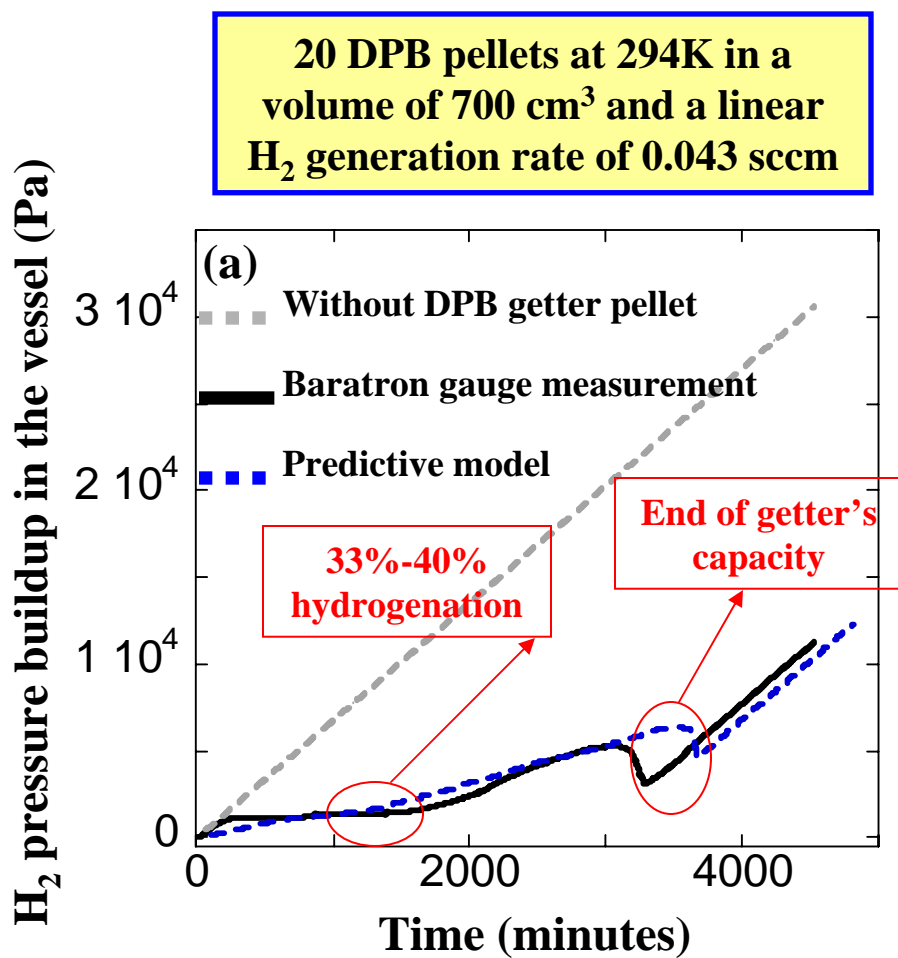


Fig. 12

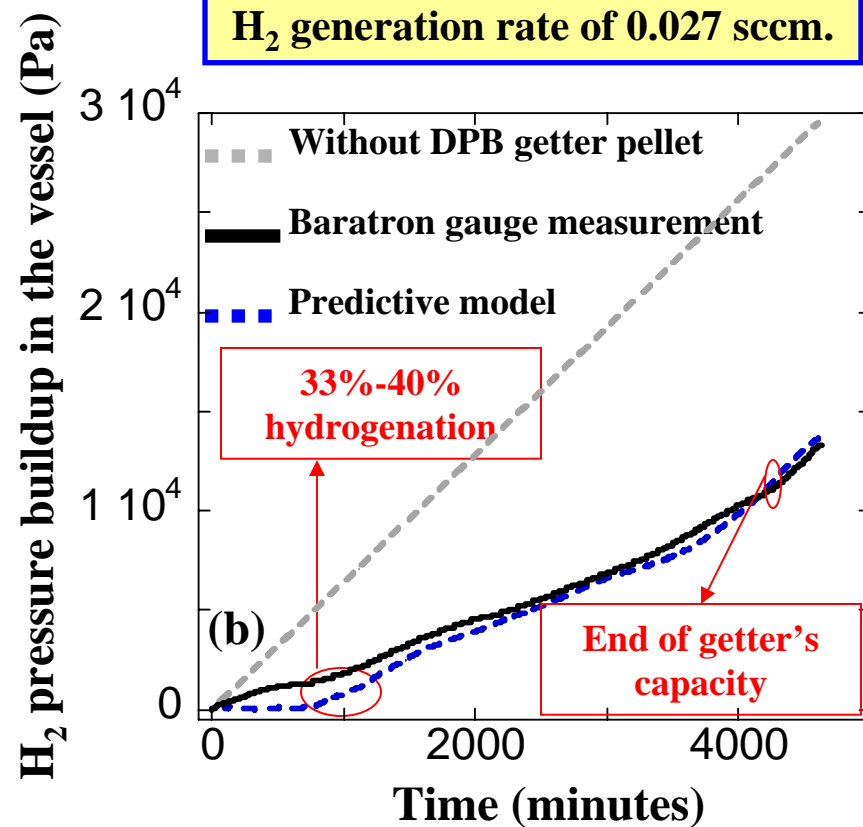
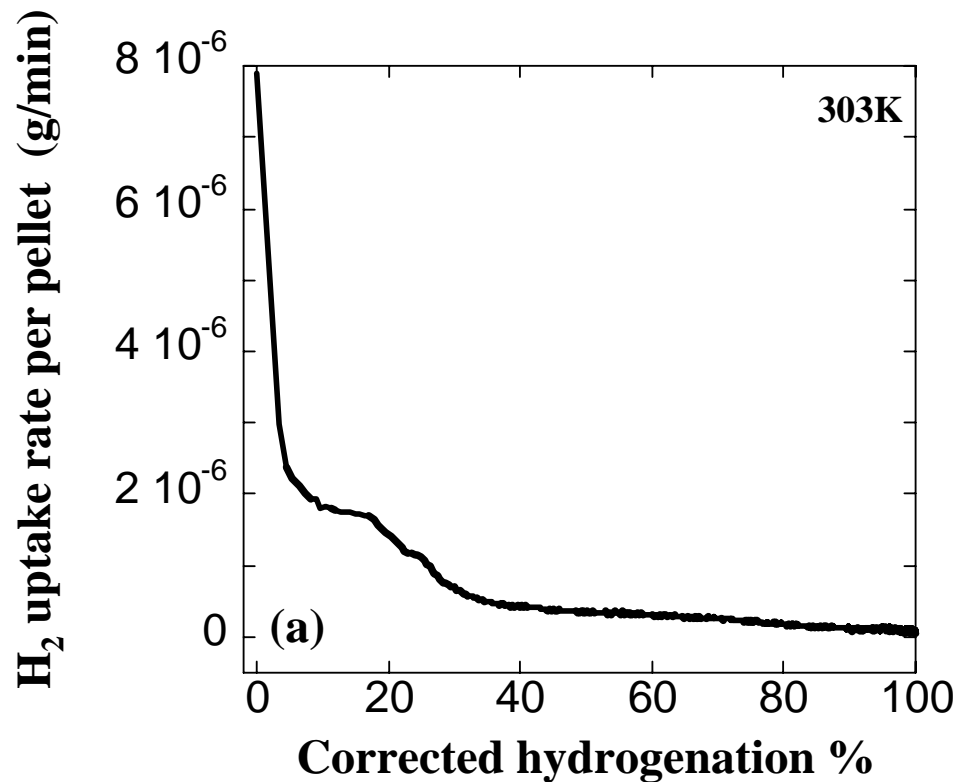


Fig. 13

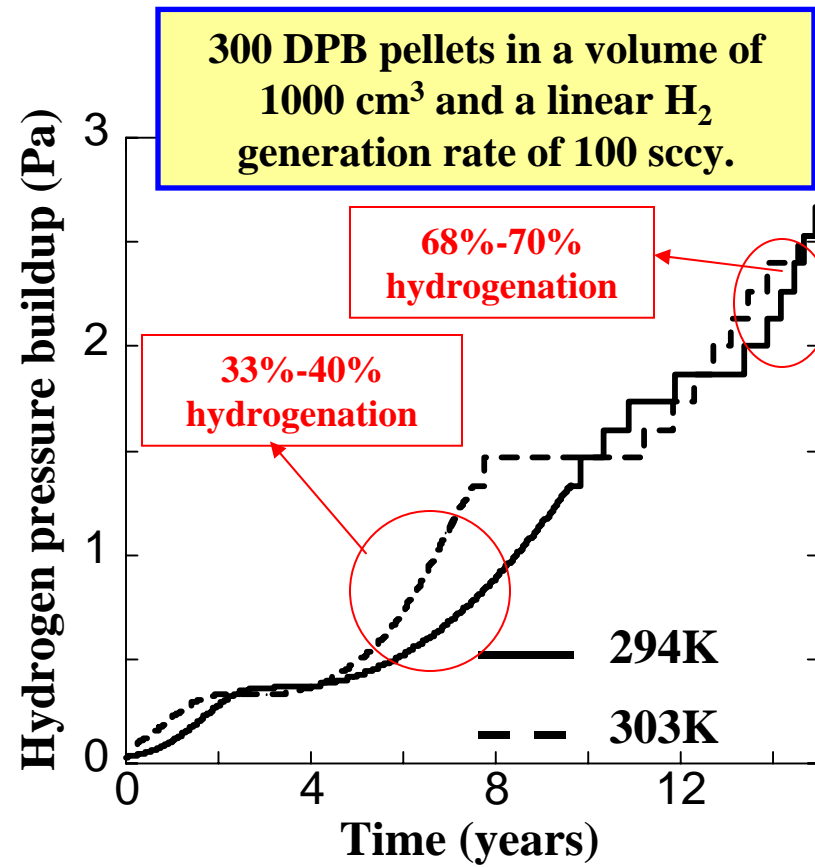


Fig. 14